Supplementary Material

Rings of Rings: Calixpyrrole Cyclotrimers

Rakia Saidi,[1,2] Franz H. Kohnke,[2*] Marco Ponassi,[3] Camillo Rosano,[3] Aldo Profumo[3]

[1]Laboratory of Organic Chemistry LR17ES08, University of Sciences of Sfax, 3000 Sfax Tunisia
[2]Dipartimento CHIBIOFARAM, Universita` di Messina, viale F. Stagno d'Alcontres, 31, 98166 Messina, Italy
[3]IRCCS Policlinico San Martino, Largo R. Benzi 10, I-16132 Genova, Italy
Email: franz@unime.it

Table of Contents

Figure S1a. ^{1}H NMR (500 MHz, $CDCl_3$) for compound **3** with resonances assignments S3
Figure S1b. ^{1}H NMR (500 MHz, $CDCl_3$) for compound **3** (Expansion) S3
Figure S1c ^{13}C NMR (125 MHz, $CDCl_3$) for compound **3** S4
Figure S1d. ESI-MS for compound **3** S4
Figure S2a. ^{1}H NMR (500 MHz, CD_2Cl_2) for compound *anti*-**4** S5
Figure S2b. ^{13}C NMR (125 MHz, CD_2Cl_2) for compound *anti*-**4** S6
Figure S2c. HSQC (CD_2Cl_2) for compound *anti*-**4** S7
Figure S2d. ESI-MS for compound *anti*-**4** S8
Figure S3a. ^{1}H NMR (500 MHz, CD_2Cl_2) for compound *syn*-**4**. S8
Figure S3b. ^{13}C NMR (125 MHz, CD_2Cl_2) for compound *syn*-**4** S9
Figure S3c. HSQC (CD_2Cl_2) for compound *syn*-**4** S10
Figure S4a. ^{1}H NMR (500 MHz, $CDCl_3$/CD_3OD 6:1) for compound *anti*-**5** S11
Figure S3d. ESI-MS for compound *syn*-**4** S11
Figure S4b. ^{13}C NMR (500 MHz, $CDCl_3$/CD_3OD 6:1) for compound *anti*-**5** S12
Figure S4c. HSQC ($CDCl_3$/CD_3OD 6:1) for compound *anti*-**5** S13
Figure S4d. ESI-MS for compound *anti*-**5**. S14
Figure S5a. ^{1}H NMR (500 MHz, $CDCl_3$/CD_3OD 6:1) for compound *syn*-**5** S14
Figure S5b. ^{13}C NMR (125 MHz, $CDCl_3$/CD_3OD 6:1) for compound *syn*-**5** S15
Figure S5c. ESI-MS for compound *syn*-**5** S15
Figure S6a ^{1}H NMR (500 MHz, CD_2Cl_2) for compound **7** S16
Figure S6b. APT ^{13}C NMR (125 MHz, CD_2Cl_2) for compound **7** S17
Figure S6c HSQC (CD_2Cl_2) for compound **7** S18
Figure S6d. ESI-MS for compound **7** S19
Figure S7a. ^{1}H NMR (500 MHz, $CDCl_3$,) for compound **8** S20
Figure S7b. ^{13}C HNMR (125 MHz, $CDCl_3$) for compound **8** S21
Figure S7c. APT ^{13}C NMR (125 MHz, $CDCl_3$) for compound **8** S22
Figure S7d. HSQC ($CDCl_3$) for compound **8** S23
Figure S7e. ^{1}H NMR (500MHz, DMSO-d_6) for compound **8** S24
Figure S8a ^{1}H NMR (500 MHz, DMSO-d_6) for compound **10** with assignments S25

Figure S8b ^{1}H NMR (500 MHz, CD_2Cl_2) for compound **10** S26
Figure S8c. COSY (500 MHz, CD_2Cl_2) Partial spectrum for compound **10** S27
Figure S8d. ^{13}C NMR (500 MHz, CD_2Cl_2) for compound **10** S28
Figure S8e. HSQC (CD_2Cl_2) for compound **10** S29
Figure S9a. ^{1}H NMR (500 MHz, CD_2Cl_2) for compound *anti-anti-anti*-**11** S30
Figure S9b. ^{1}H NMR COSY (500 MHz, CD_2Cl_2) Partial spectrum for compound *anti-anti-anti*-**11** S30
Figure S9c. ^{13}C NMR (125 MHz, CD_2Cl_2) for compound *anti-anti-anti*-**11** S31
Figure S9d. HSQC (CD_2Cl_2) for compound *anti-anti-anti*-**11** S32
Figure S9e. ESI-MS for compound *anti-anti-anti*-**11** S33
Figure S10a. ^{1}H NMR (500 MHz, DMSO-d_6) for *syn-syn-syn*-**11** S34
Figure S10b. ^{1}H NMR (500 MHz, DMSO-d_6) for *syn-syn-syn*-**11** S35
Figure S10c. ^{13}C NMR (125 MHz, DMSO-d_6) for *syn-syn-syn*-**11** S36
Figure S10d. ESI-MS for *syn-syn-syn*-**11** S36
Figure S11a. ^{1}H NMR (DMSO-d_6) for 1,3-dichloro-4,6-dinitrobenzene **9** S37

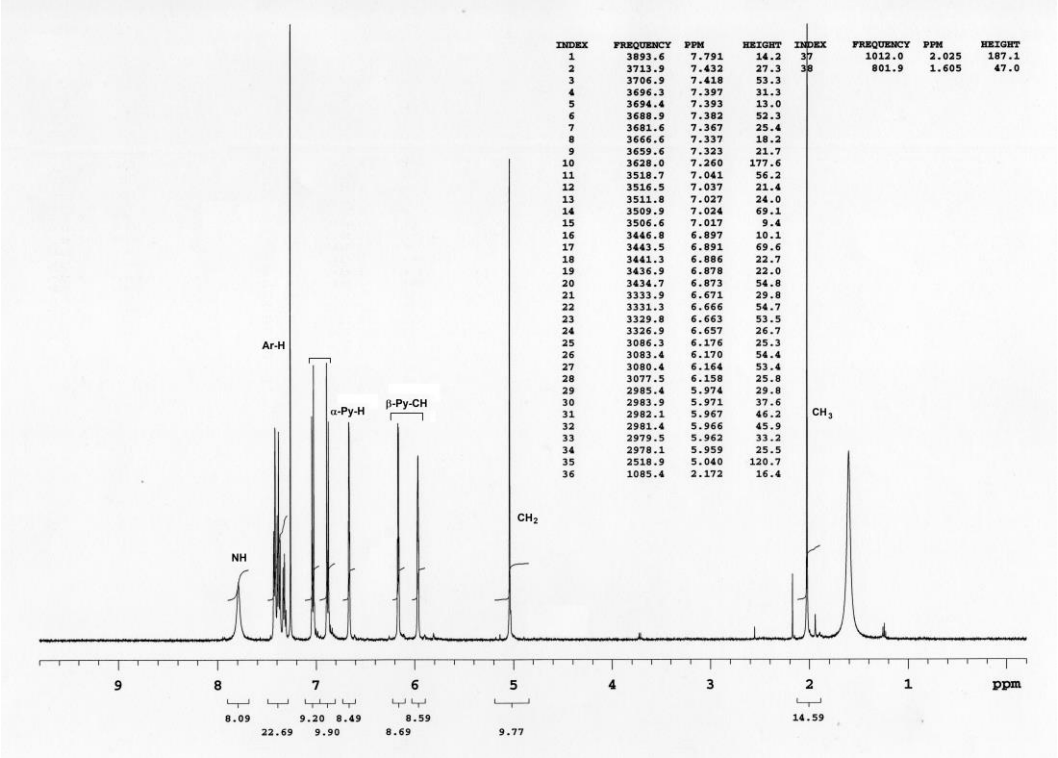

Figure S1a. ^{1}H NMR (500 MHz, $CDCl_3$) for compound **3** with resonances assignments.

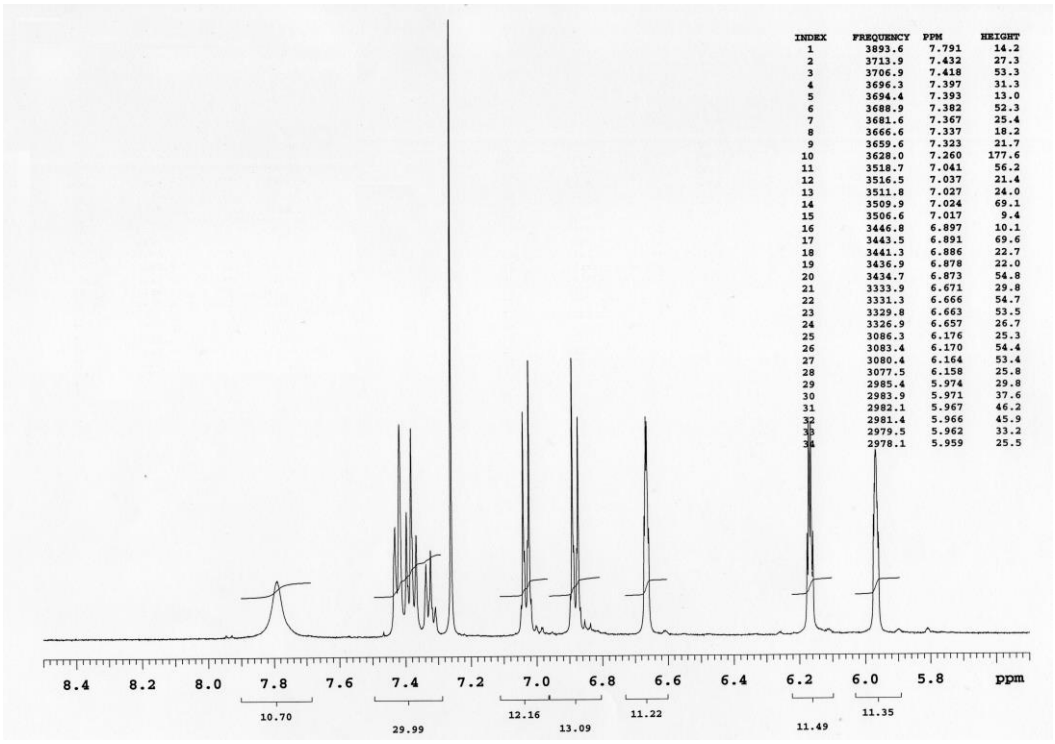

Figure S1b. ^{1}H NMR (500 MHz, $CDCl_3$) for compound **3** (Expansion).

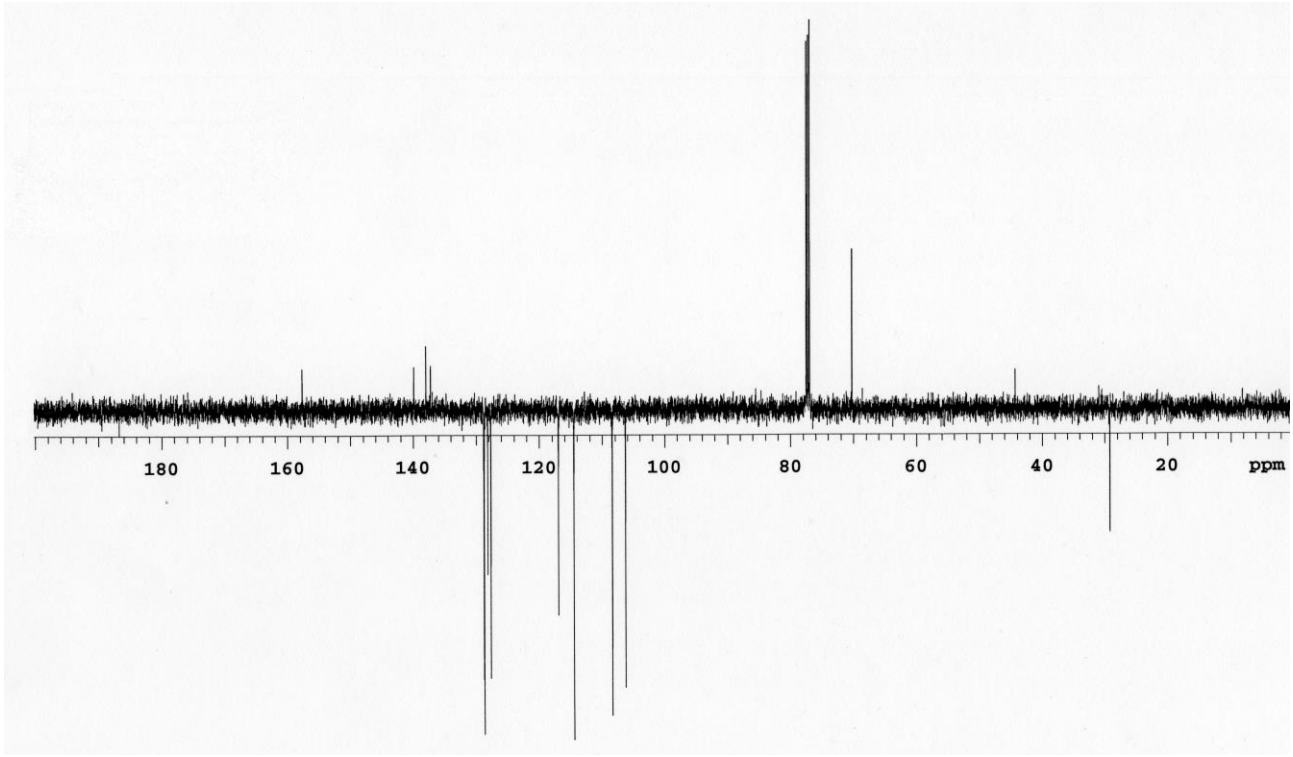

Figure S1c ^{13}C NMR (125 MHz, $CDCl_3$) for compound **3.**

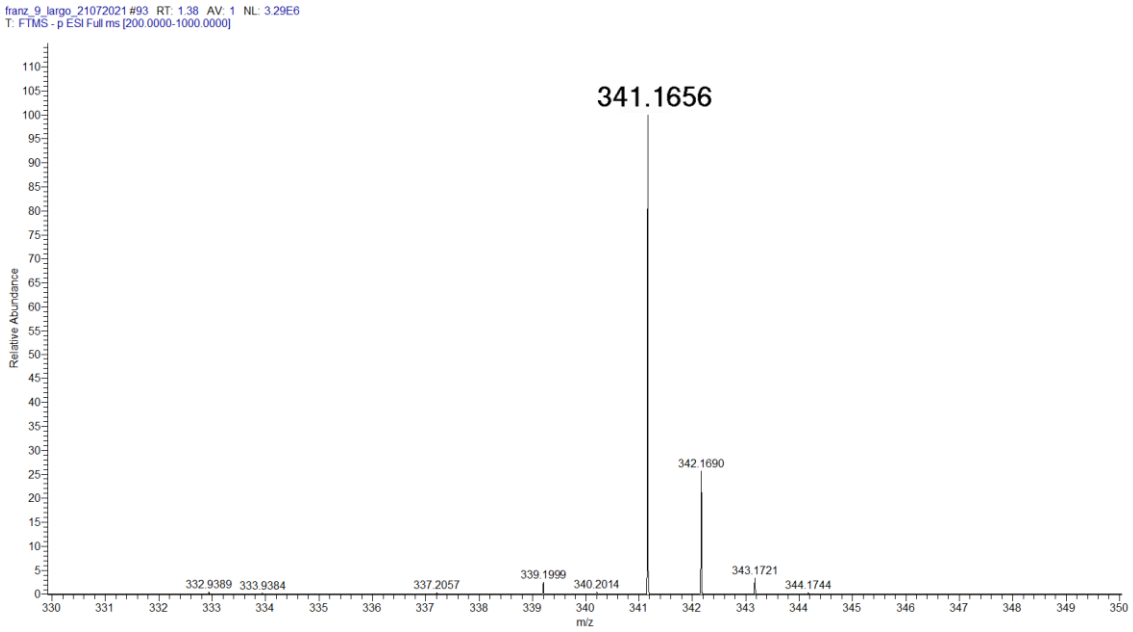

Figure S1d. ESI-MS for compound **3**. Calc. *m/z* for $C_{23}H_{20}N_2O_2$ 342.1732.

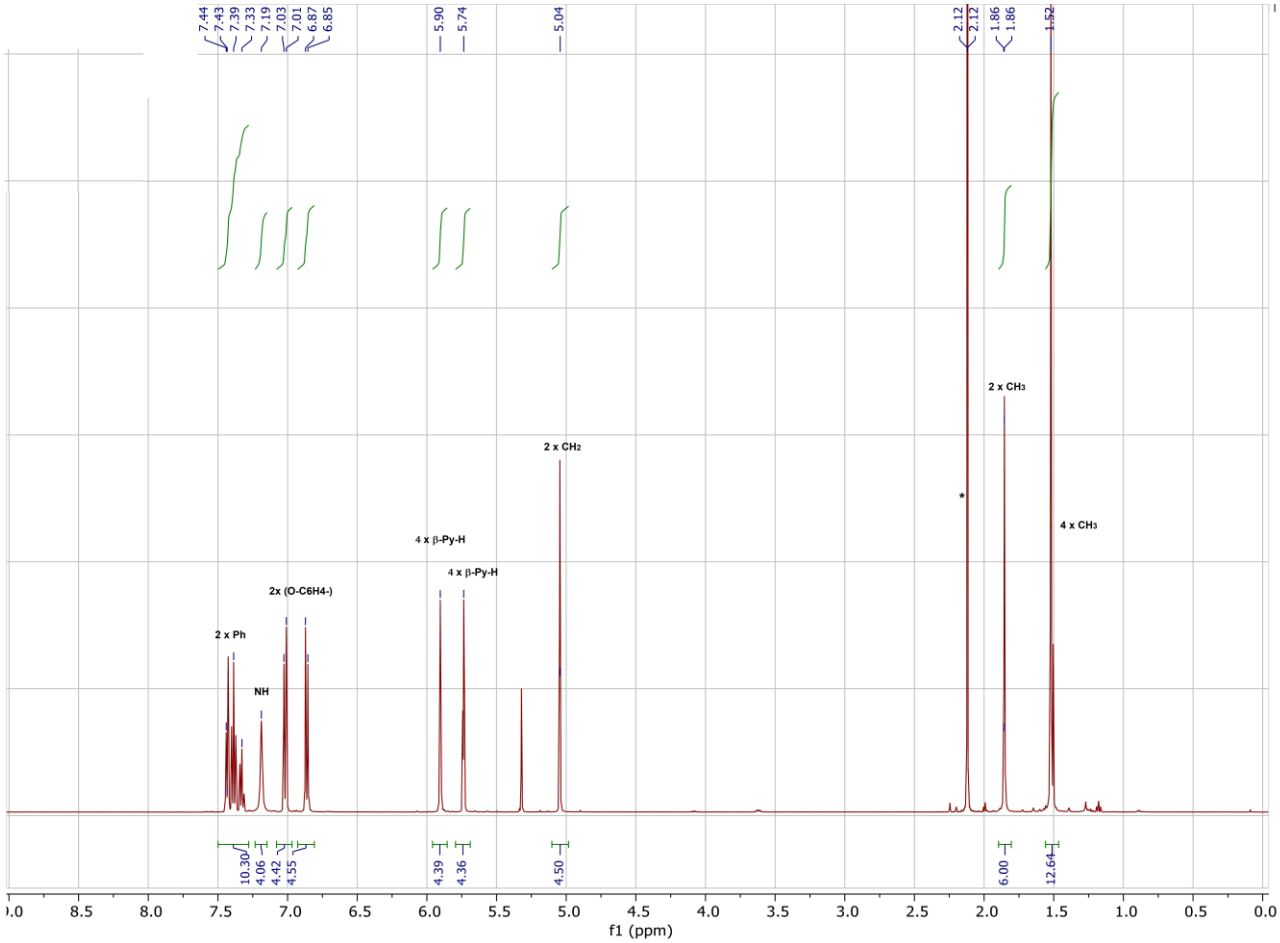

Figure S2a. ^{1}H NMR (500 MHz, CD_2Cl_2) for compound *anti*-**4** with resonances assignments. * Adventitious water.

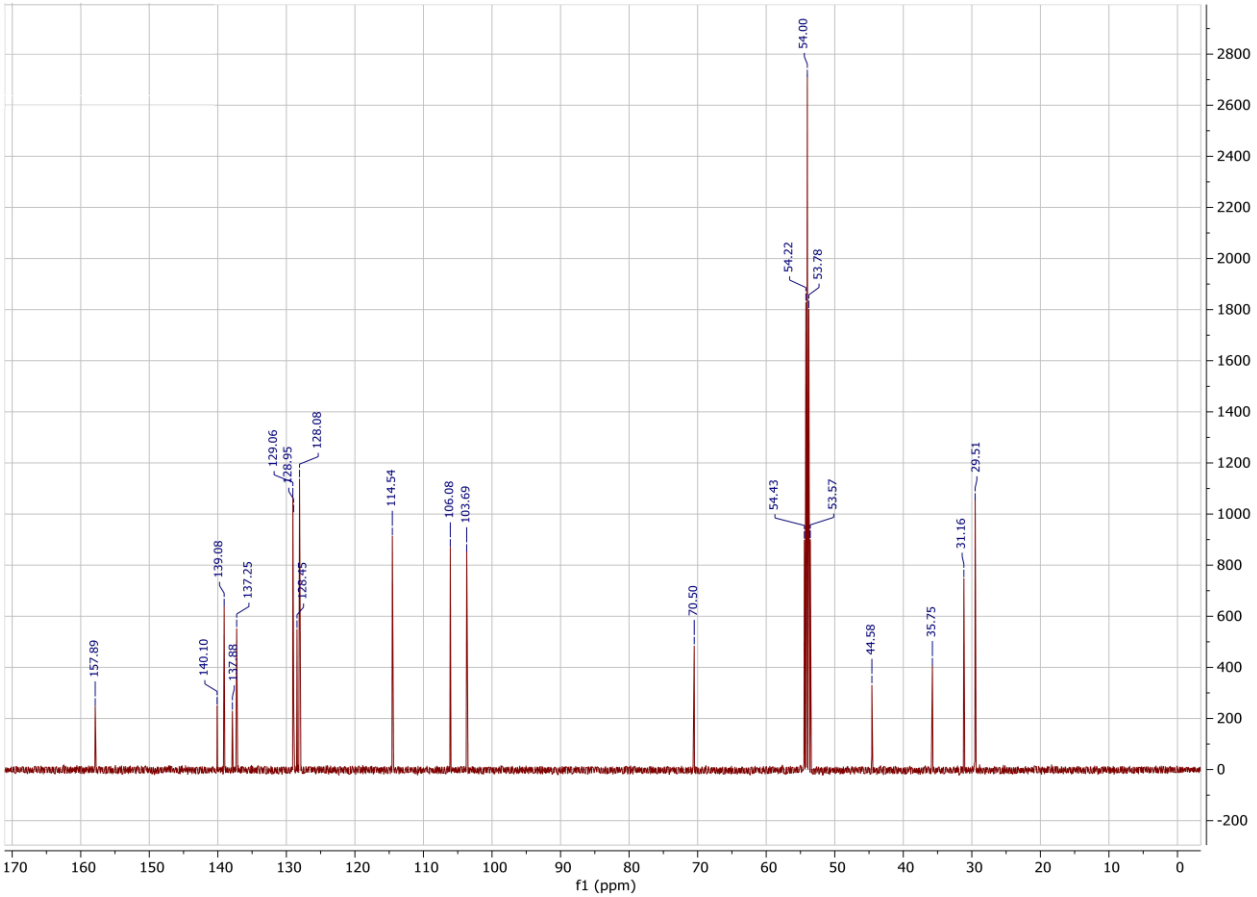

Figure S2b. ^{13}C NMR (125 MHz, CD_2Cl_2) for compound *anti*-**4.**

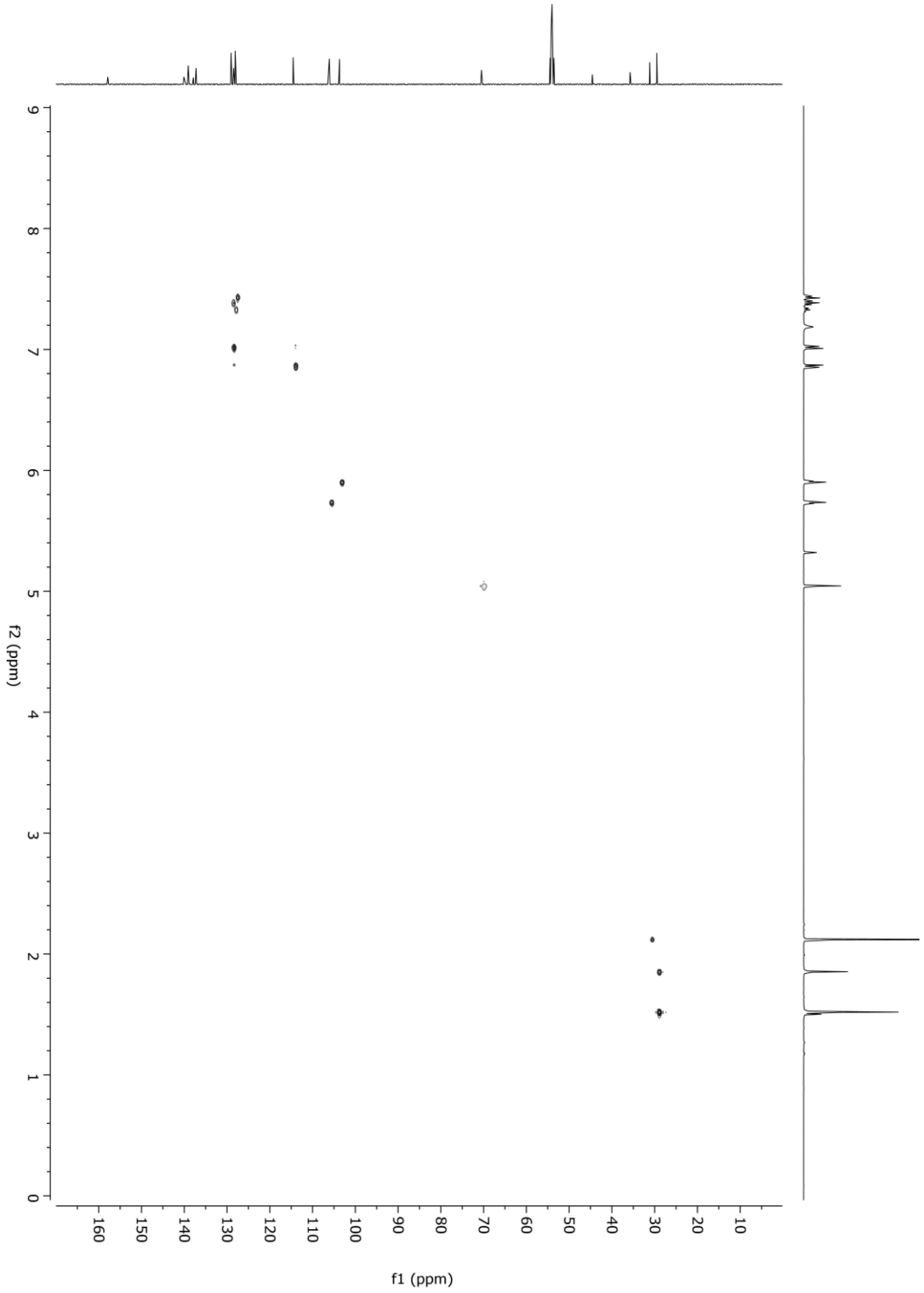

Figure S2c. HSQC (CD_2Cl_2) for compound *anti*-**4.**

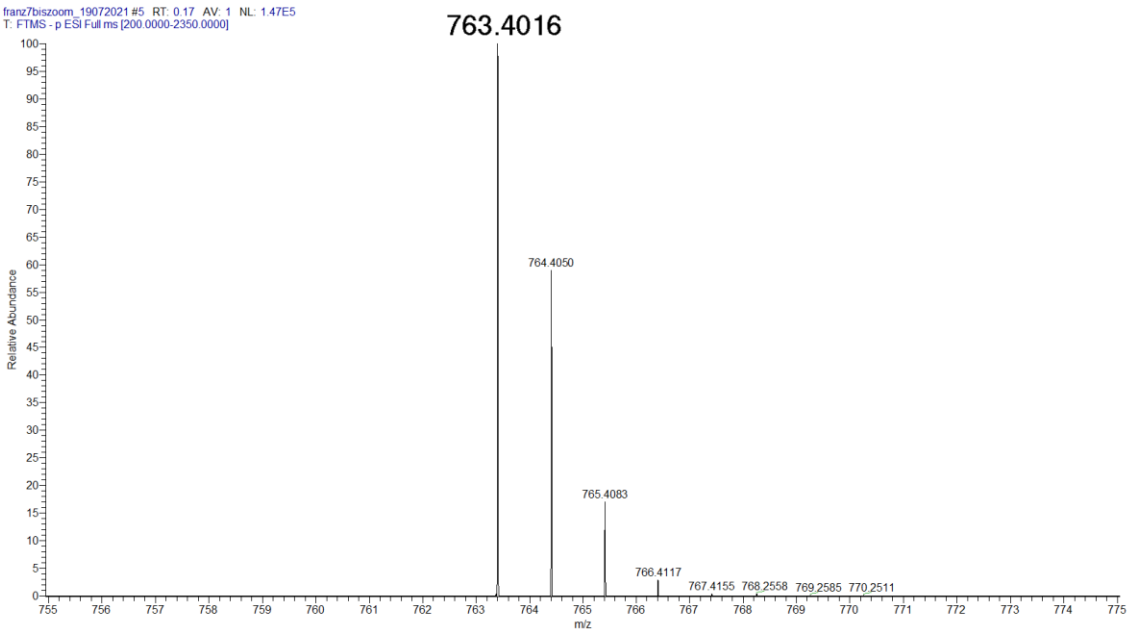

Figure S2d. ESI-MS for compound *anti*-**4**. Calc. *m/z* for $C_{52}H_{52}N_4O_2$ 764.4090.

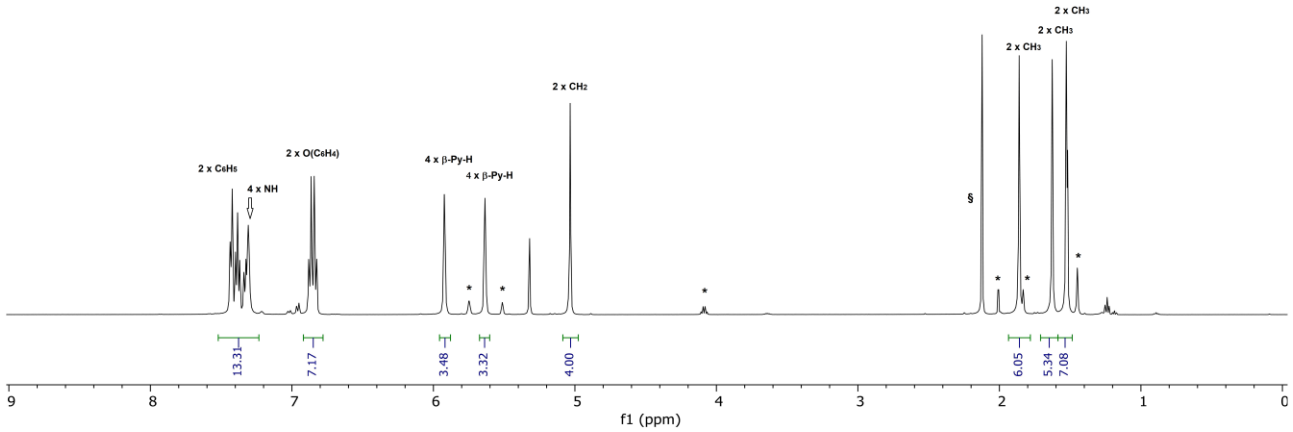

Figure S3a. ^{1}H NMR (500 MHz, CD_2Cl_2) for compound *syn*-**4** with resonances assignments. (*) Impurities from solvent; (§) water.

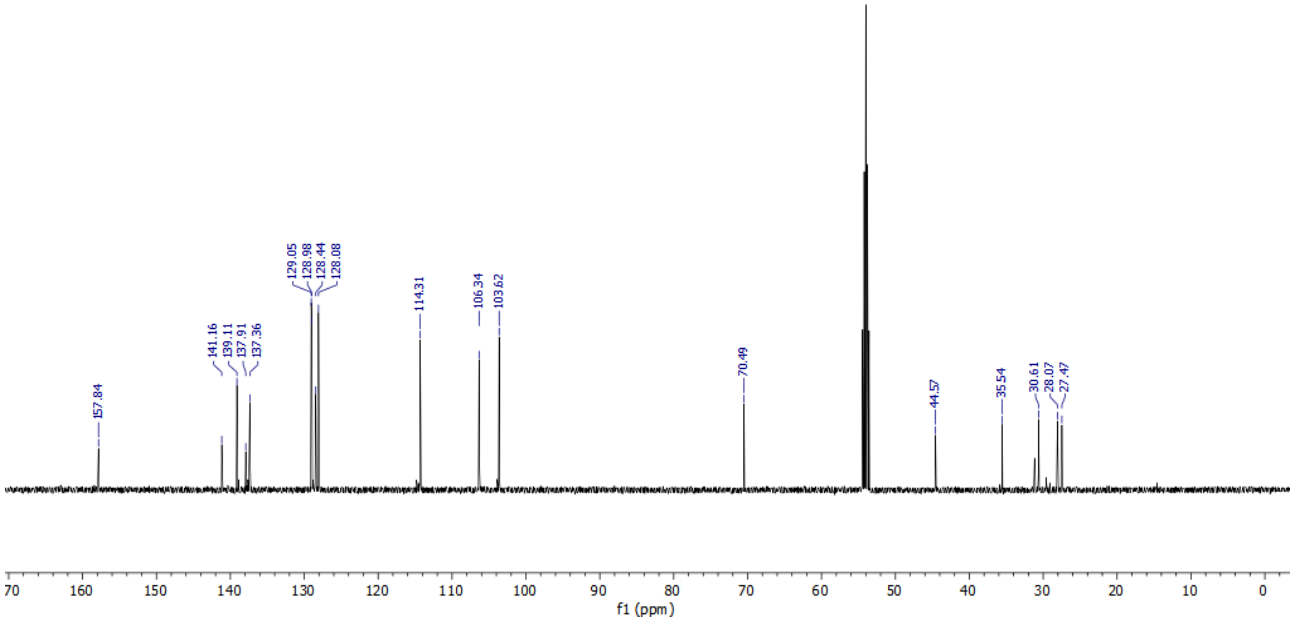

Figure S3b. ^{13}C NMR (125 MHz, CD_2Cl_2) for compound *syn*-**4.**

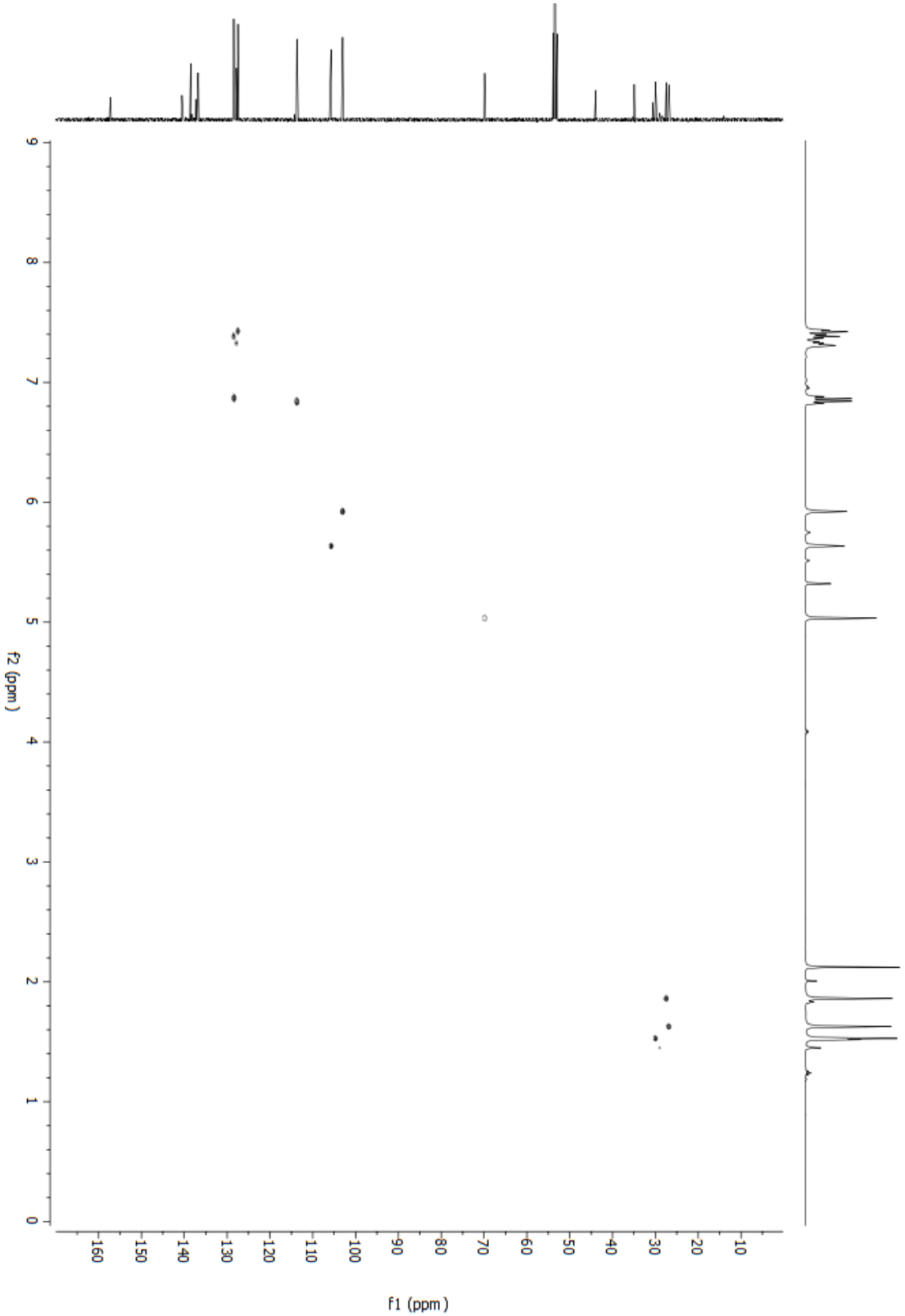

Figure S3c. HSQC (CD_2Cl_2) for compound *syn*-**4.**

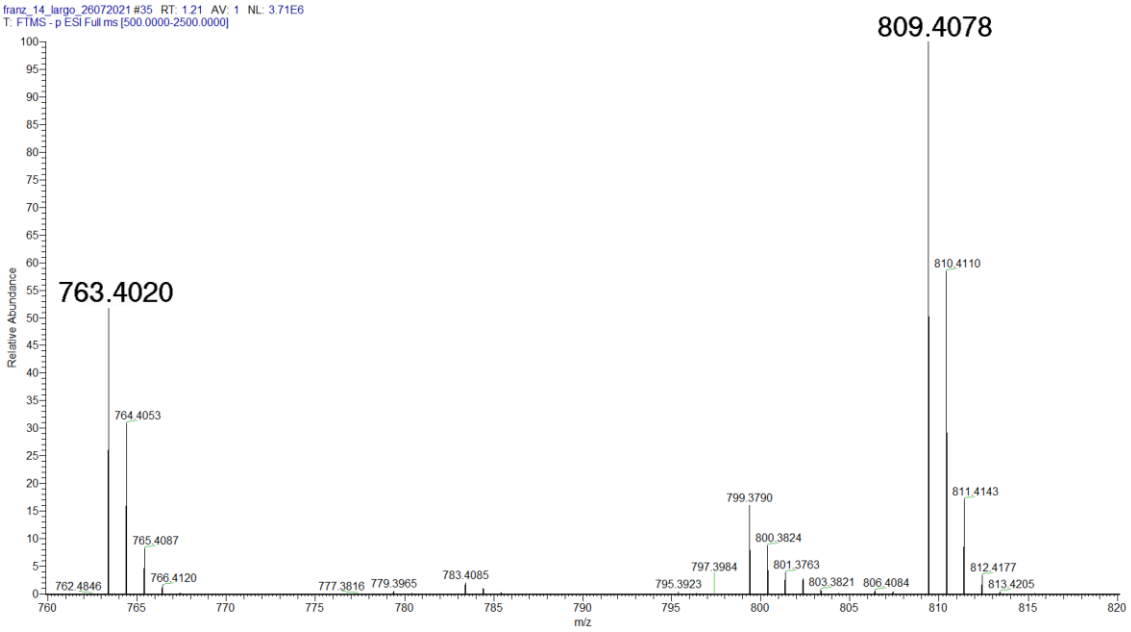

Figure S3d. ESI-MS for compound *syn*-**4**. Calc. *m/z* for $C_{52}H_{52}N_4O_2$ 764.4090; (calc. for M+[$HCOO^-$]: 809.4066).

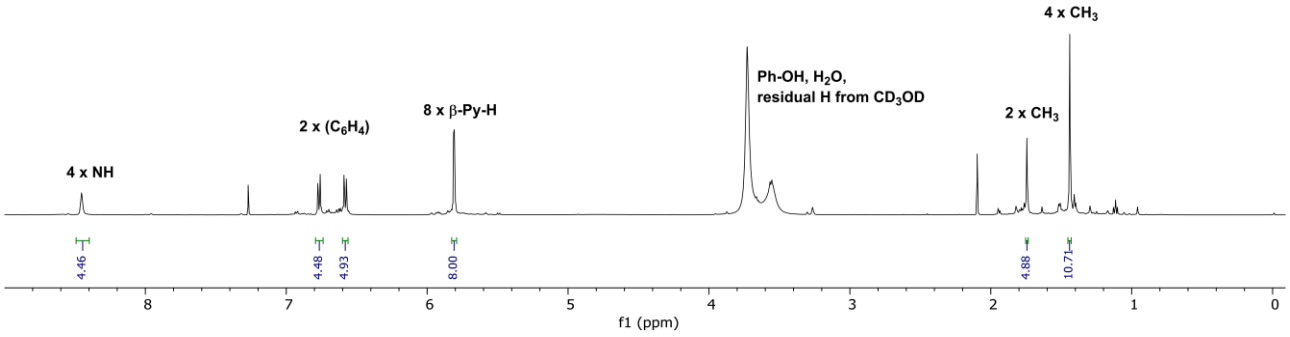

Figure S4a. ^{1}H NMR (500 MHz, $CDCl_3/CD_3OD$ 6:1) for compound *anti*-**5** with assignments.

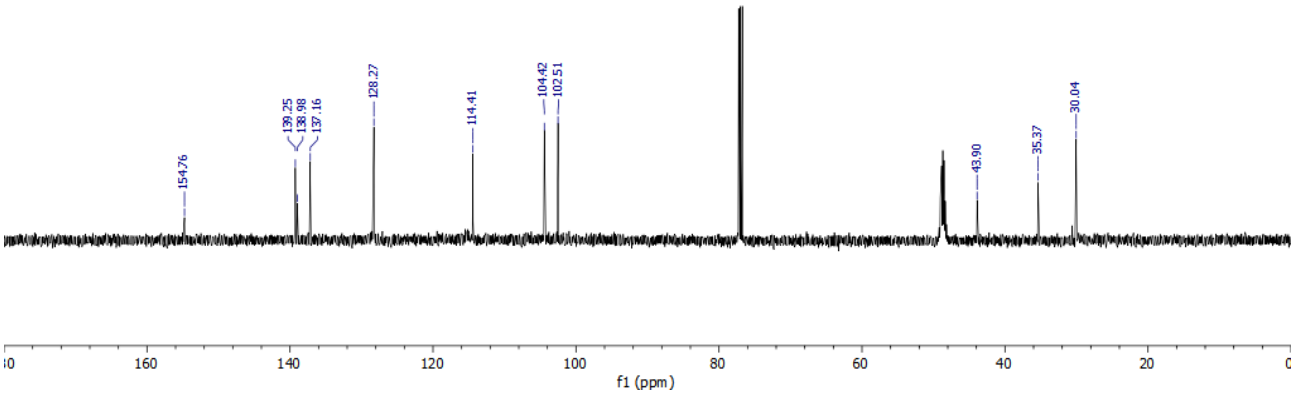

Figure S4b. ^{13}C NMR (500 MHz, $CDCl_3/CD_3OD$ 6:1) for compound *anti*-**5.**

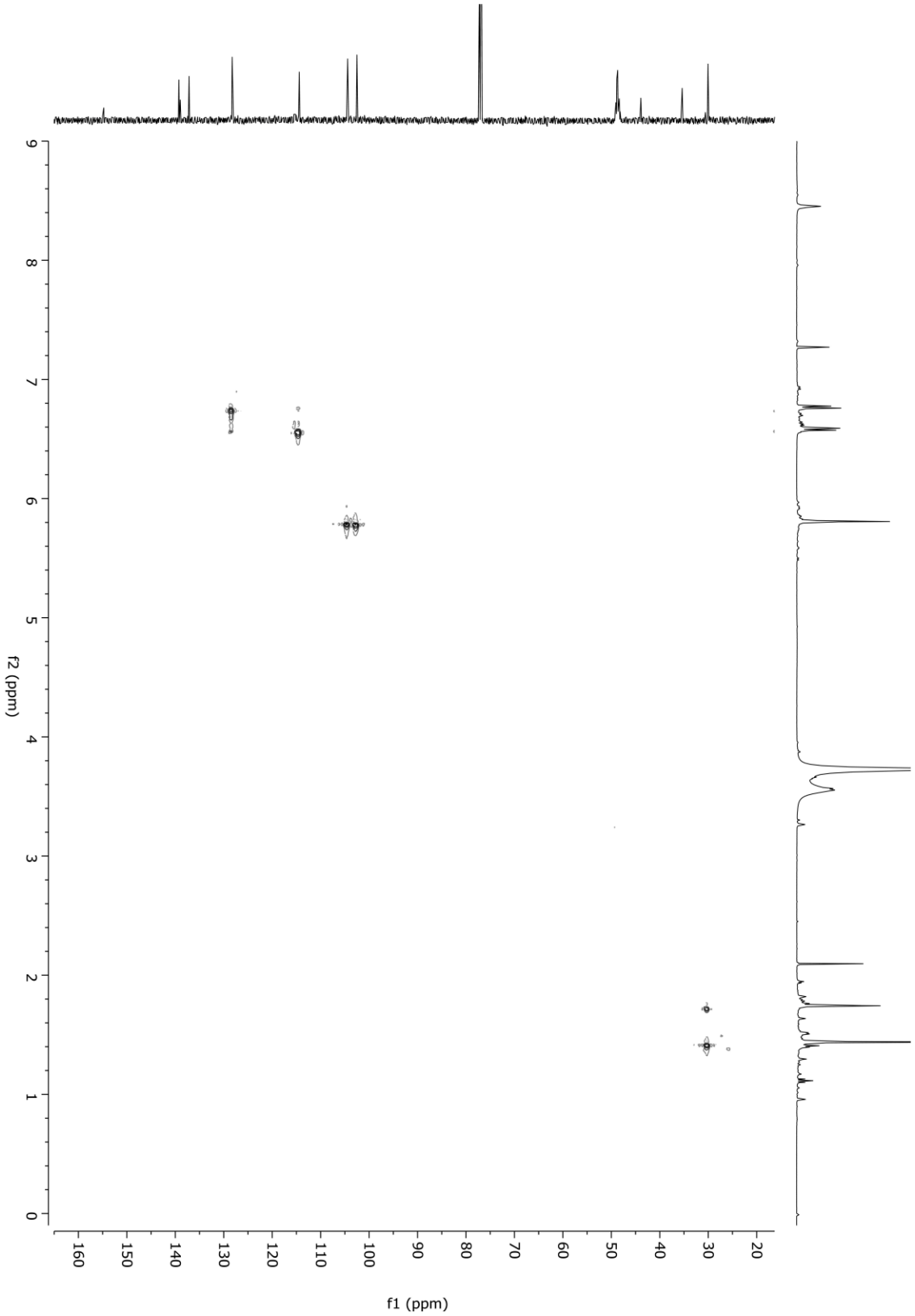

Figure S4c. HSQC ($CDCl_3$/CD_3OD 6:1) for compound *anti*-**5.**

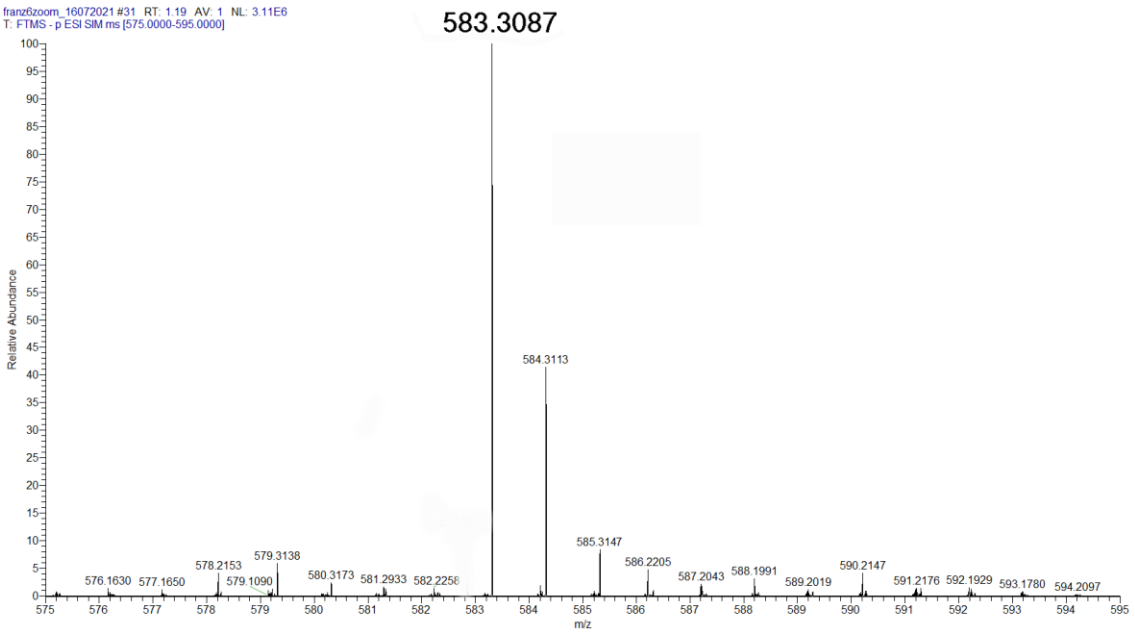

Figure S4d. ESI-MS for compound *anti*-**5**. Calc. *m/z* for $C_{38}H_{40}N_4O_2$ 584.3151.

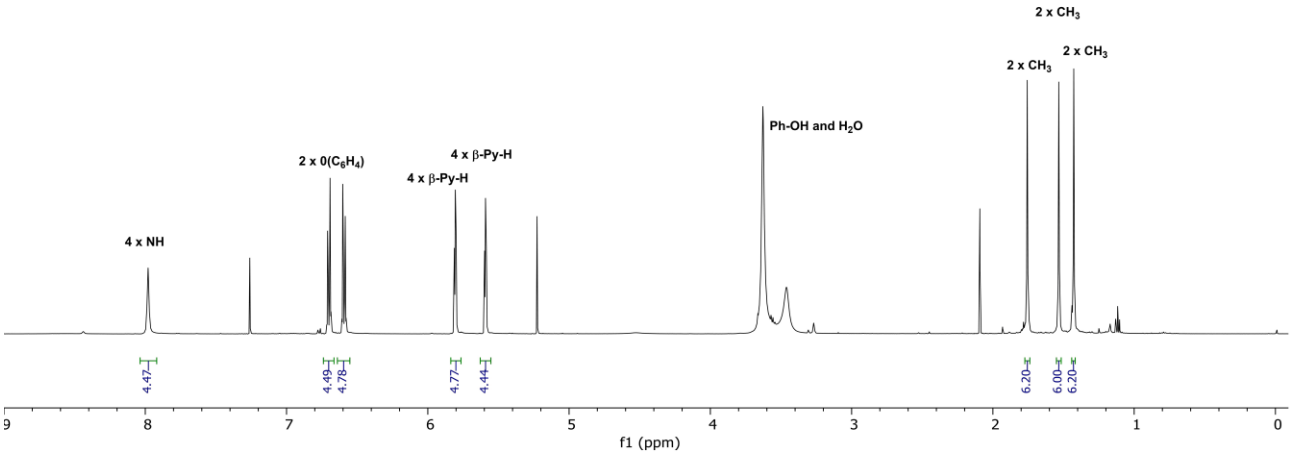

Figure S5a. ^{1}H NMR (500 MHz, $CDCl_3/CD_3OD$ 6:1) for compound *syn*-**5** with resonances assignments.

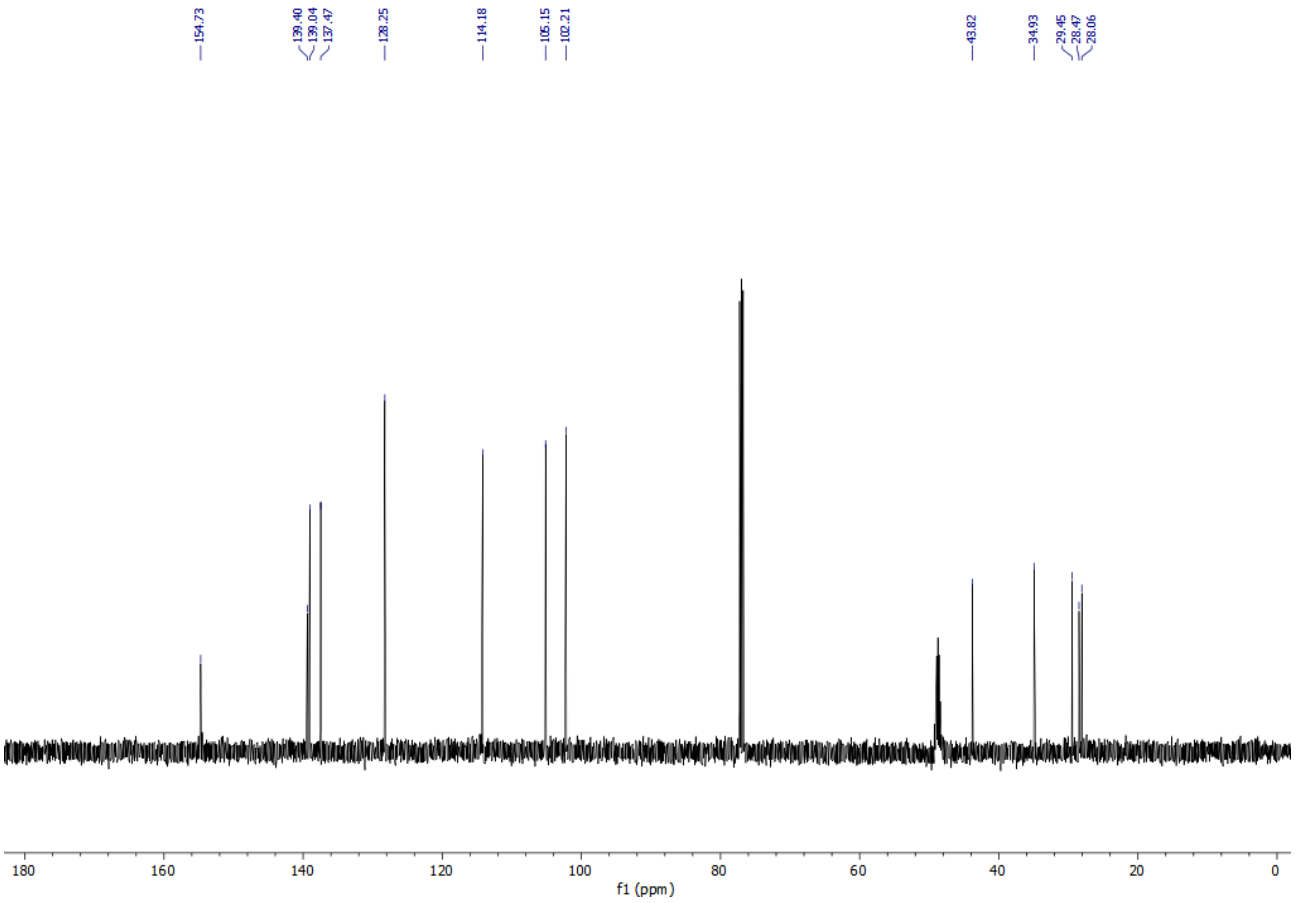

Figure S5b. ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$ 6:1) for compound *syn*-**5.**

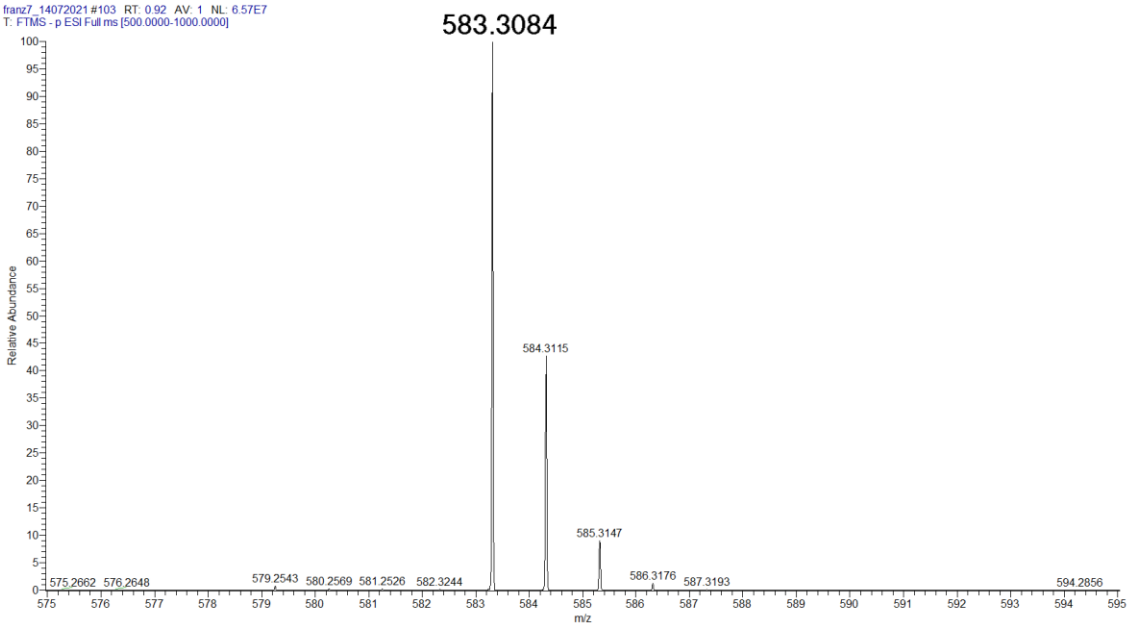

Figure S5c. ESI-MS for compound *syn*-**5**. Calc. *m/z* for $C_{38}H_{40}N_4O_2$ 584.3151.

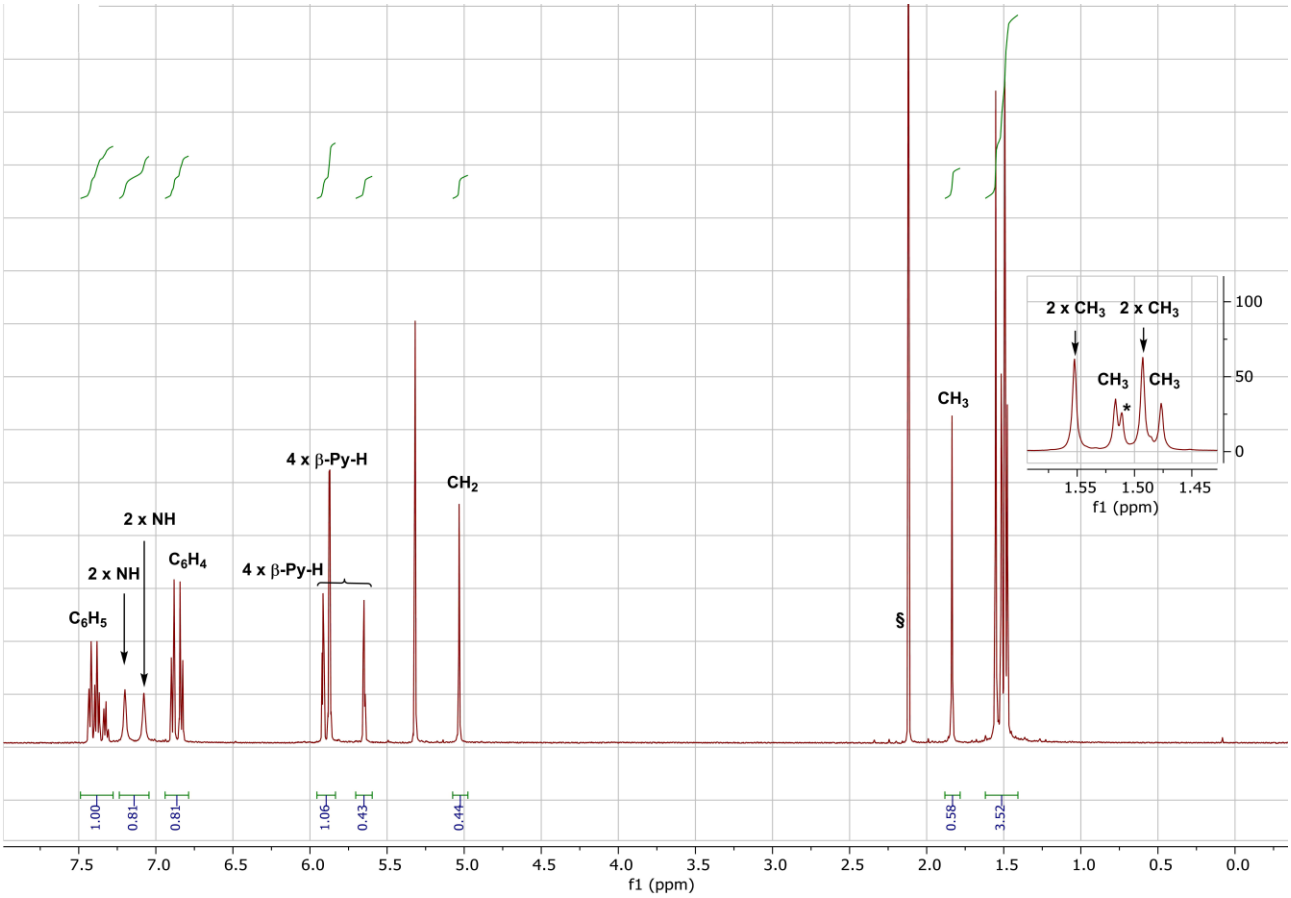

Figure S6a ^{1}H NMR (500 MHz, CD_2Cl_2) for compound **7**. § Adventitious water; * solvent impurity.

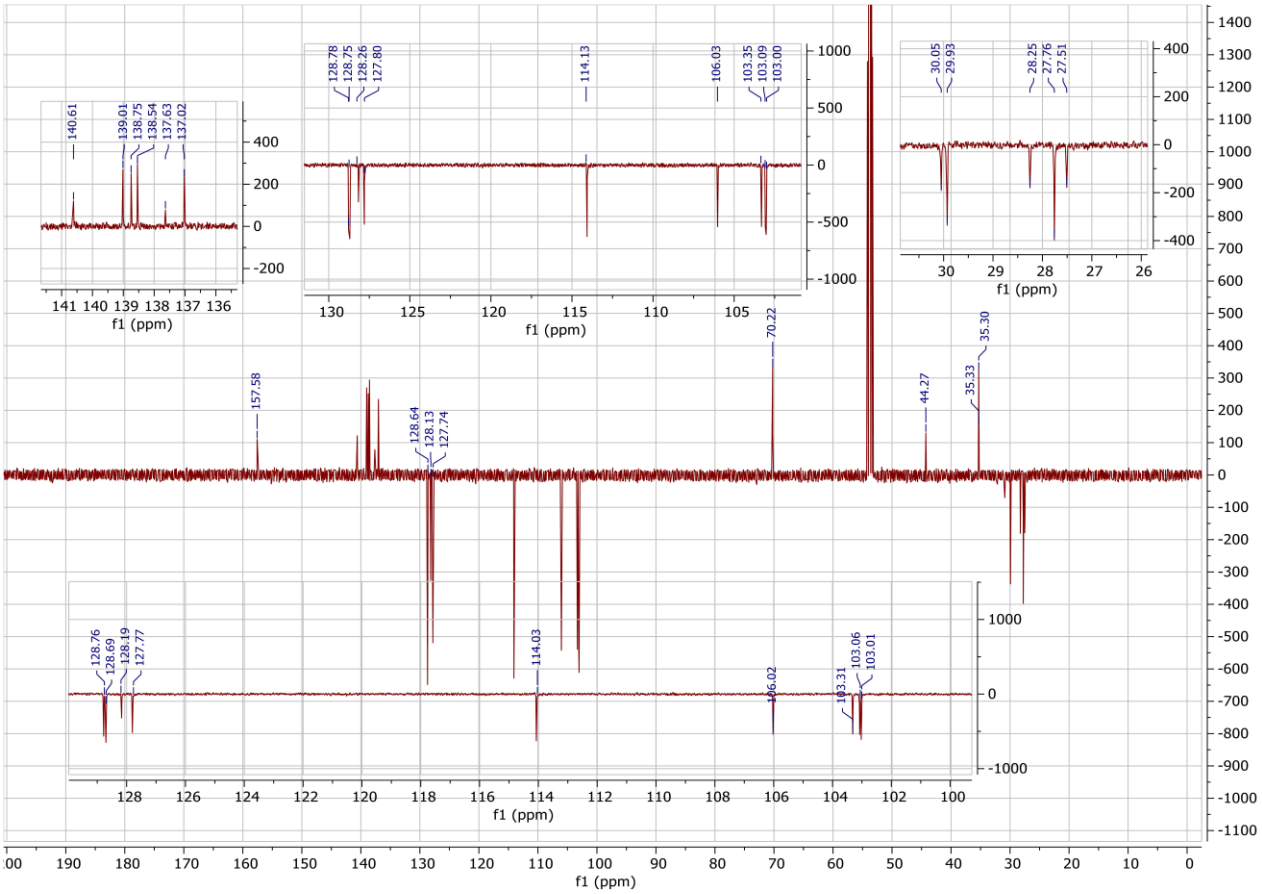

Figure S6b. APT ^{13}C NMR (125 MHz, CD_2Cl_2) for compound **7**.

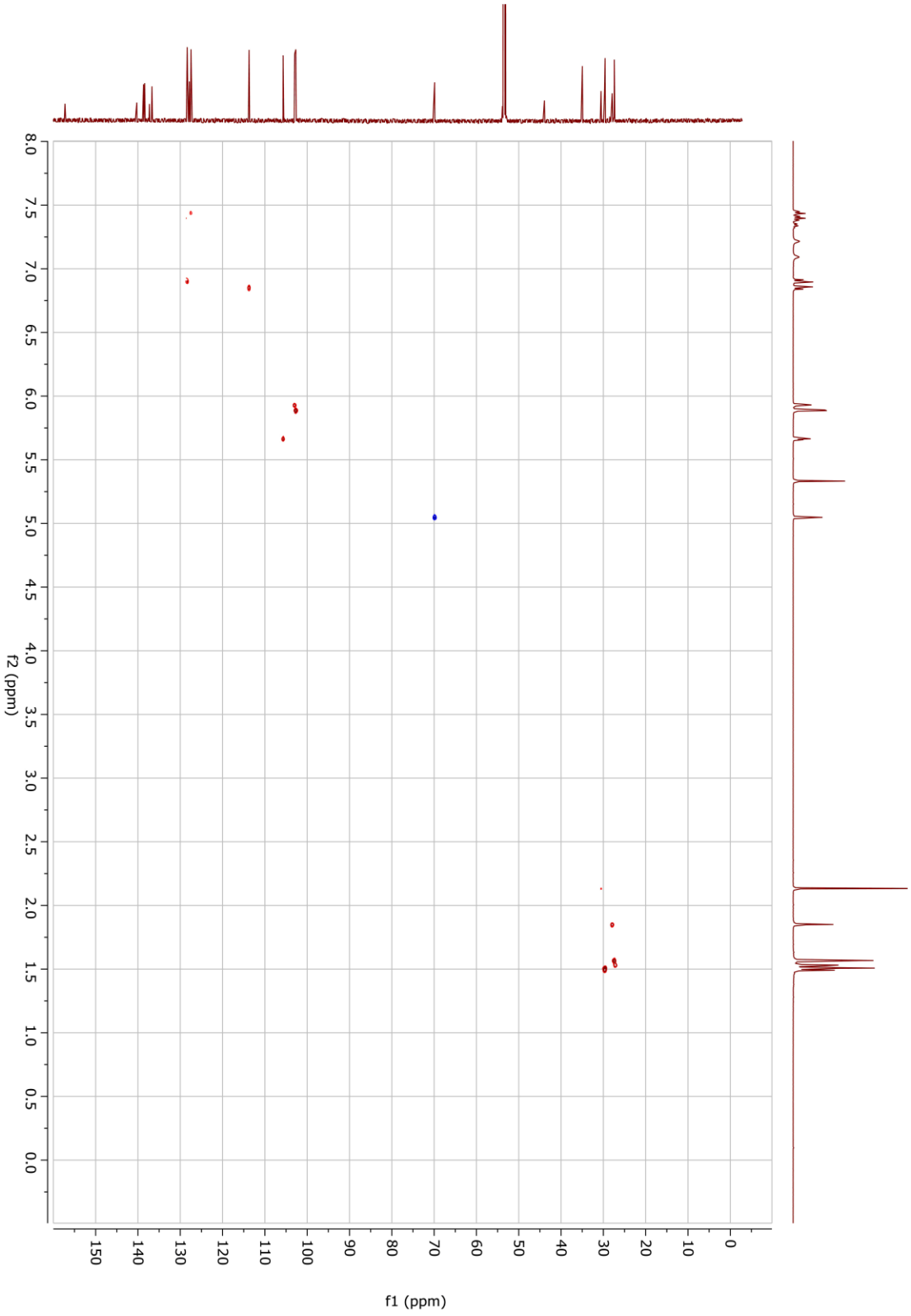

Figure S6c. HSQC (CD_2Cl_2) for compound **7.**

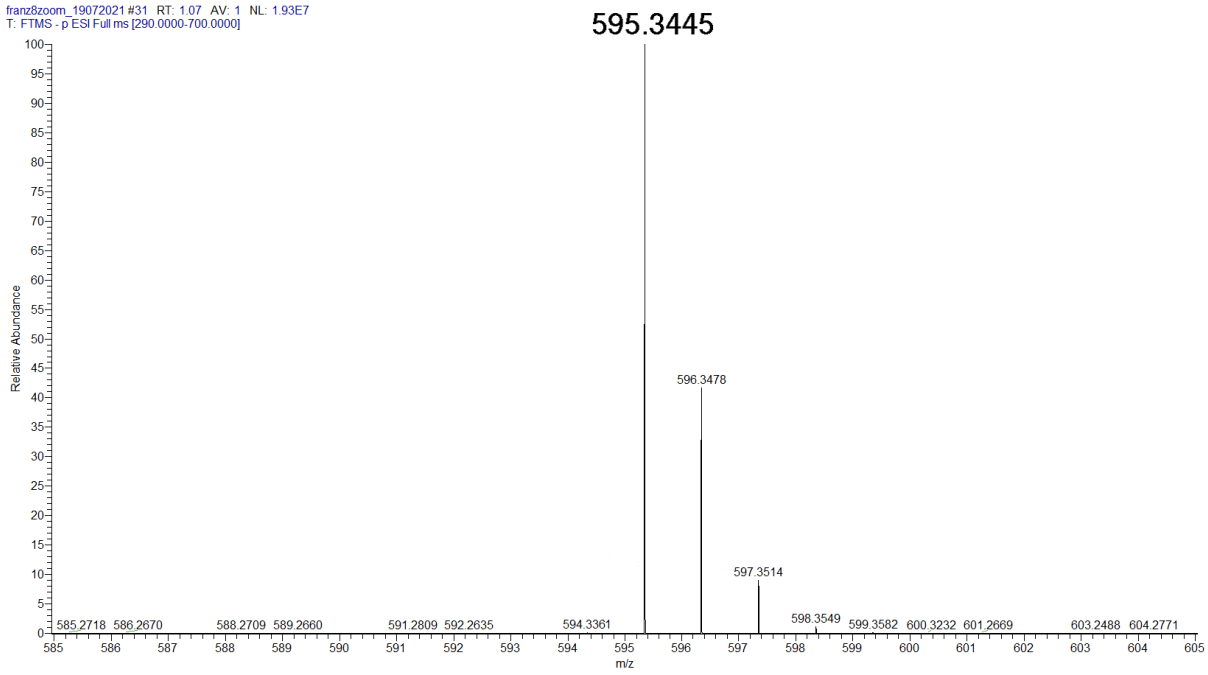

Figure S6d. ESI-MS for compound **7**. Calc. *m/z* for $C_{40}H_{44}N_4O$: 596.3515.

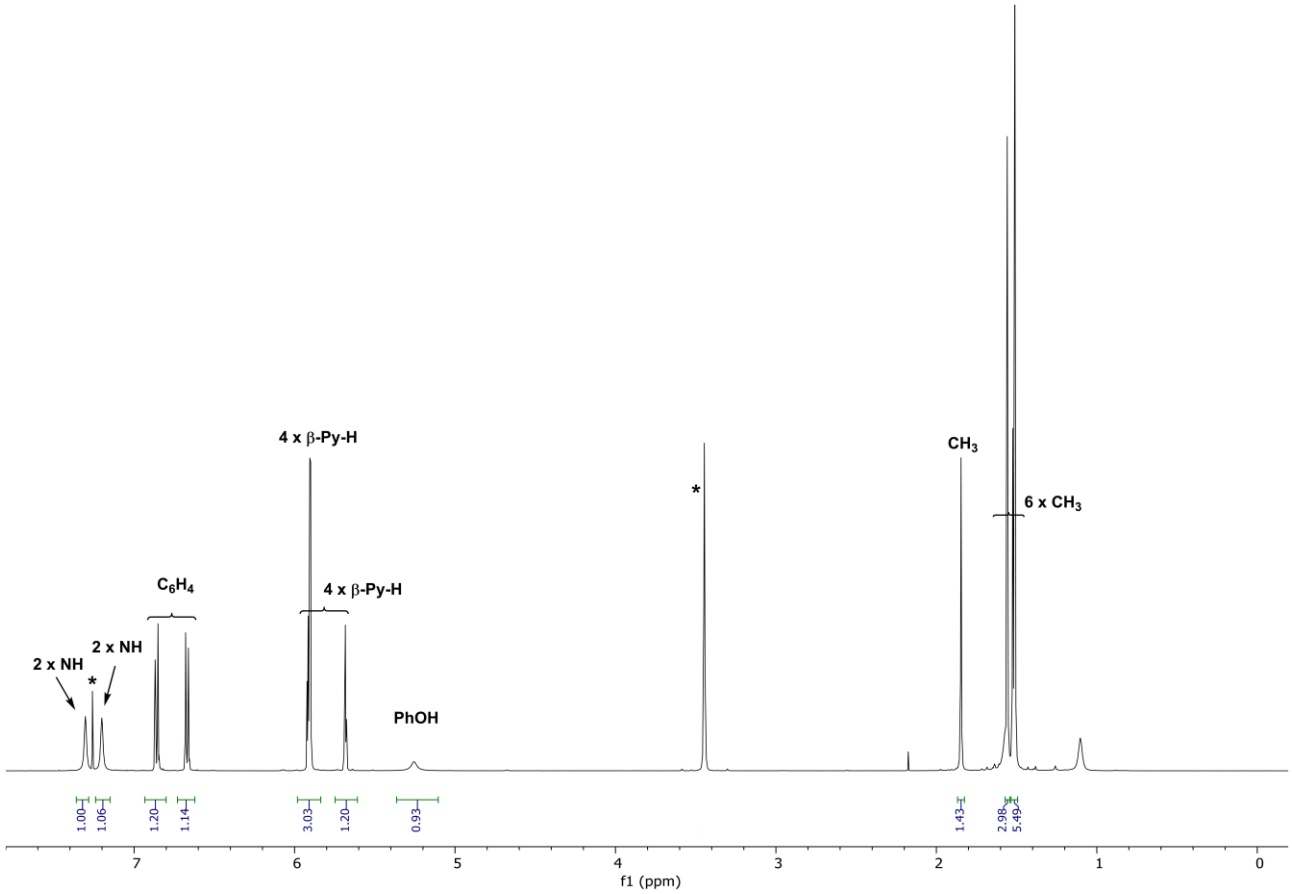

Figure S7a. ^{1}H NMR (500 MHz, $CDCl_3$,) for compound **8.** *MeOH solvent.

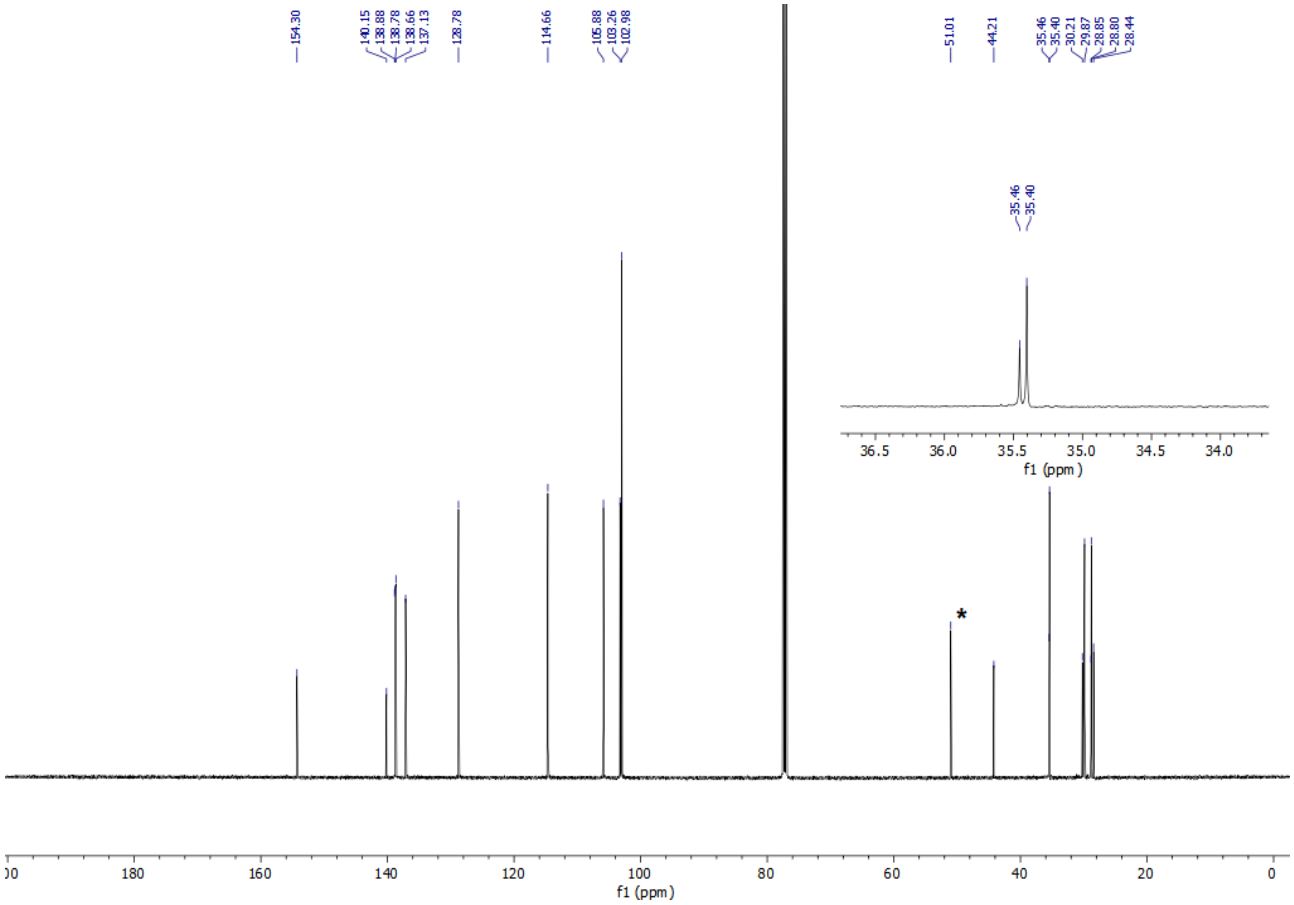

Figure S7b. ^{13}C HNMR (125 MHz, $CDCl_3$) for compound **8.** * Methanol.

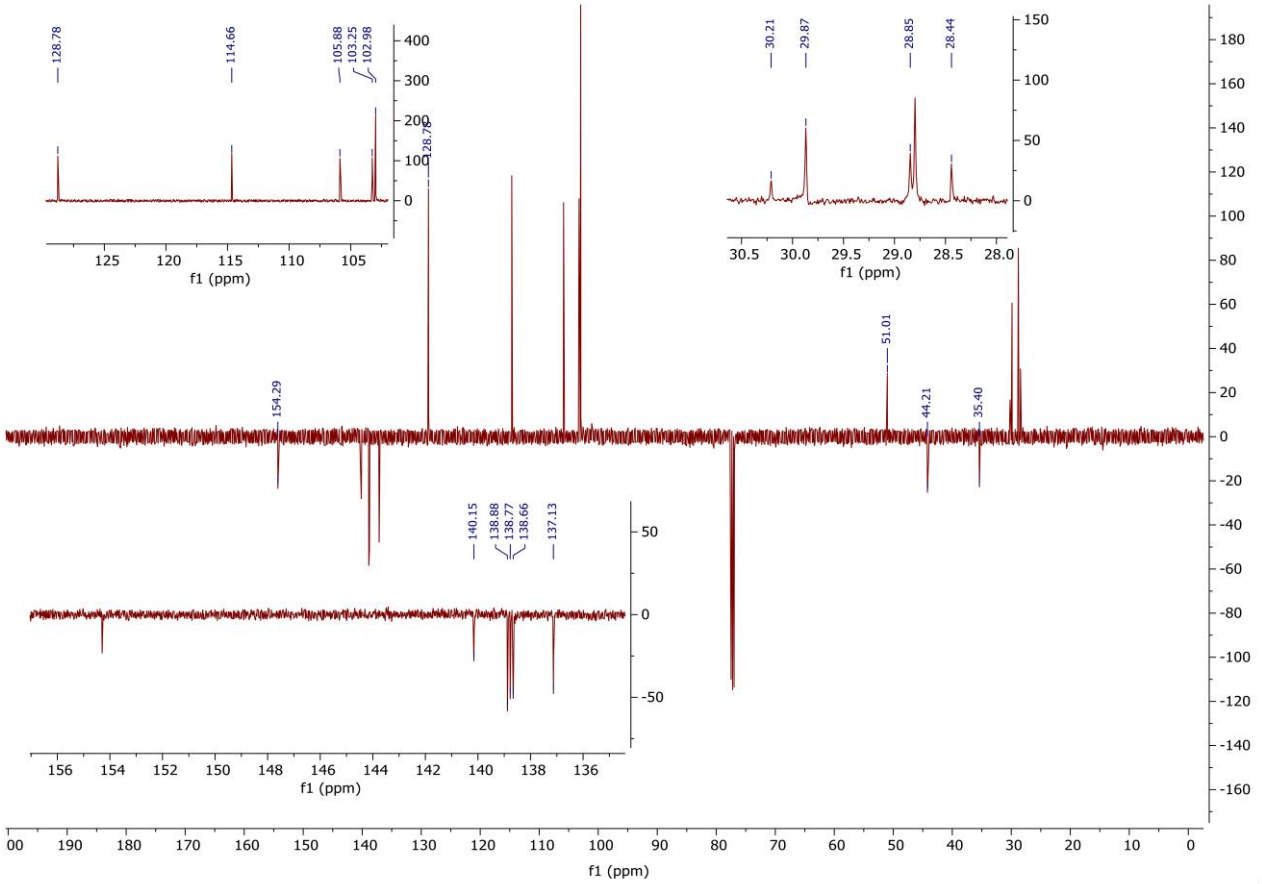

Figure S7c. APT ^{13}C NMR (125 MHz, $CDCl_3$) for compound **8.** * Methanol; the two quaternary carbon atoms at 35.4 ppm are not resolved ad resonate a single signal.

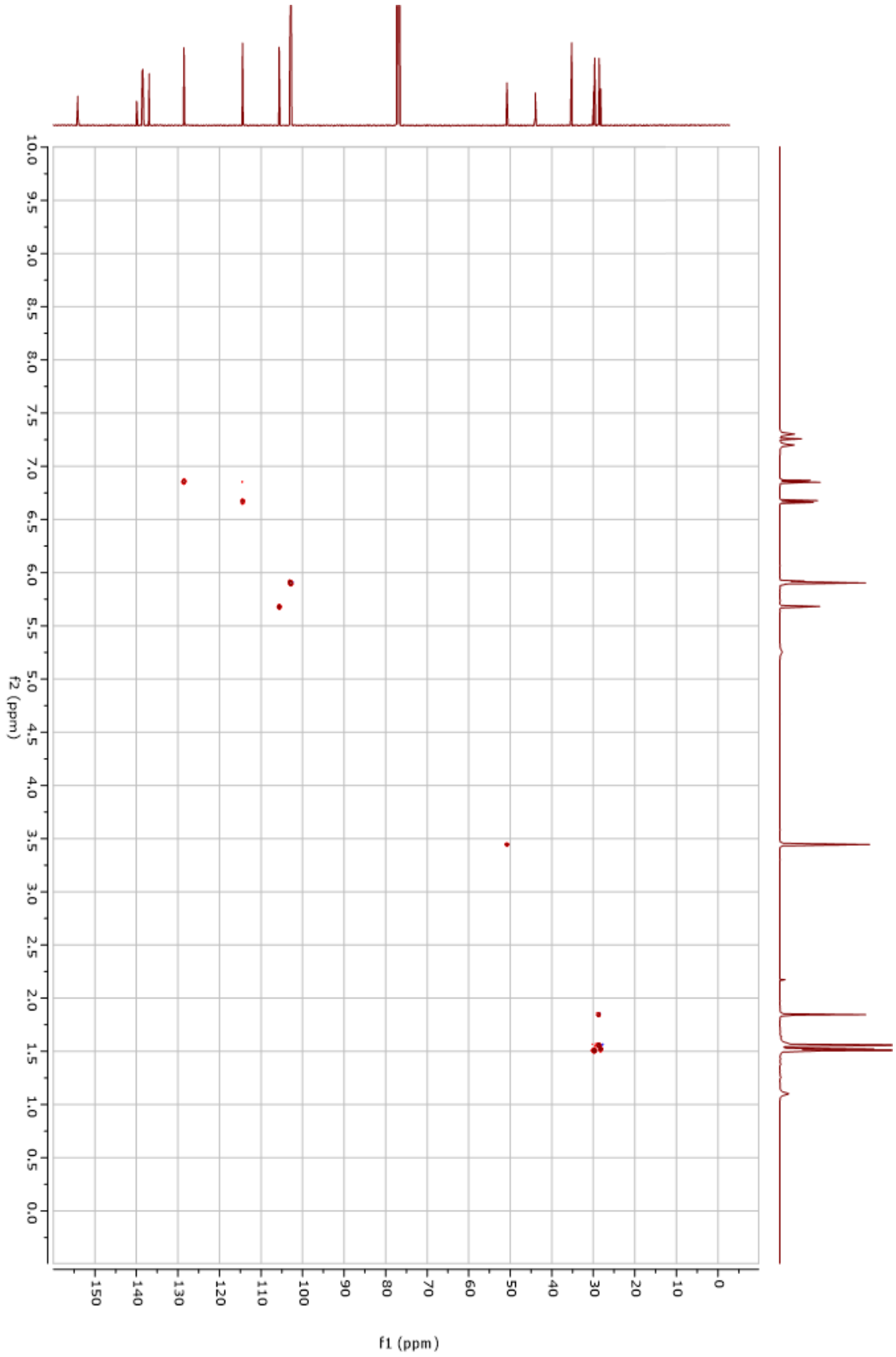

Figure S7d. HSQC ($CDCl_3$) for compound **8.**

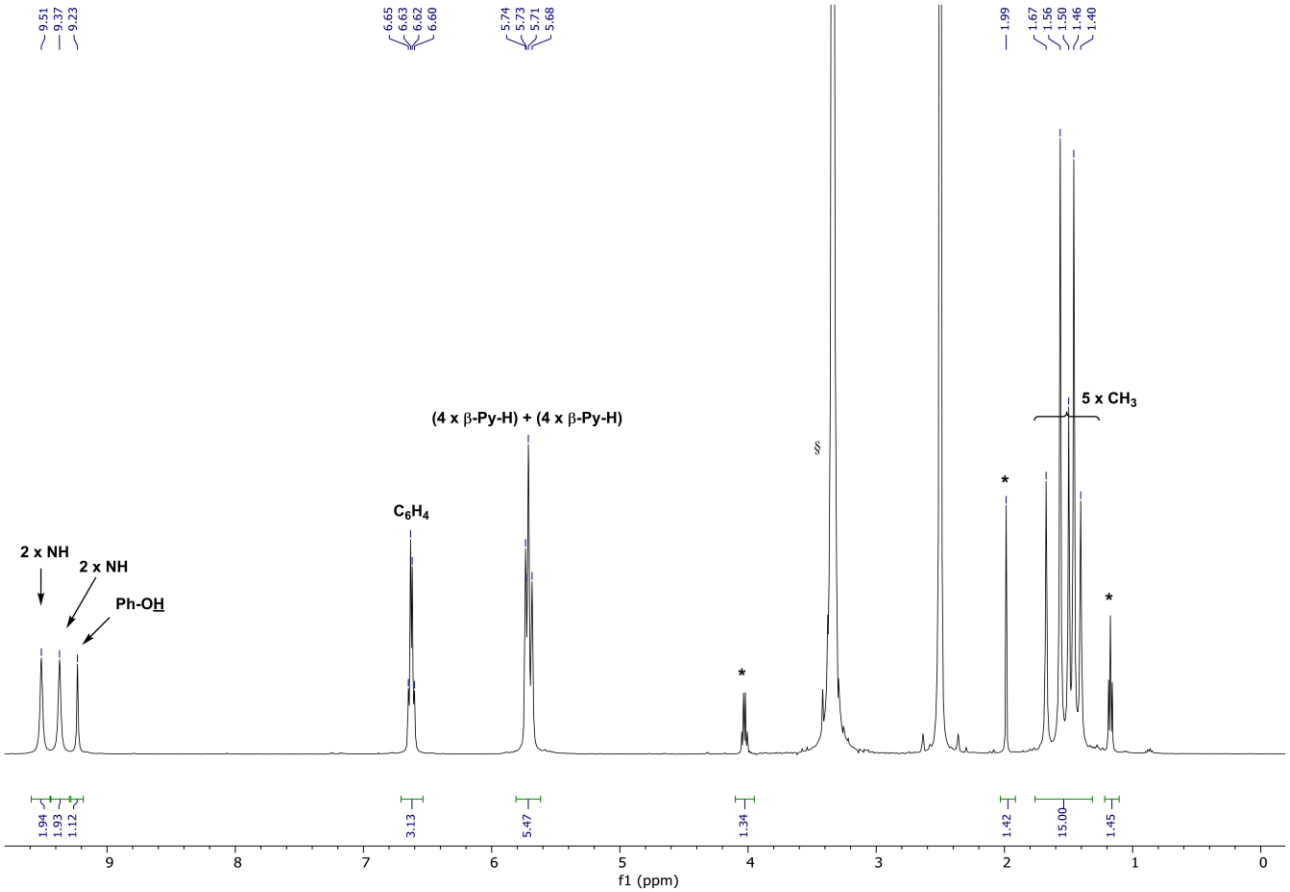

Figure S7e. ^{1}H NMR (500MHz, DMSO-d_6) for compound **8**. * Ethyl acetate, § water.

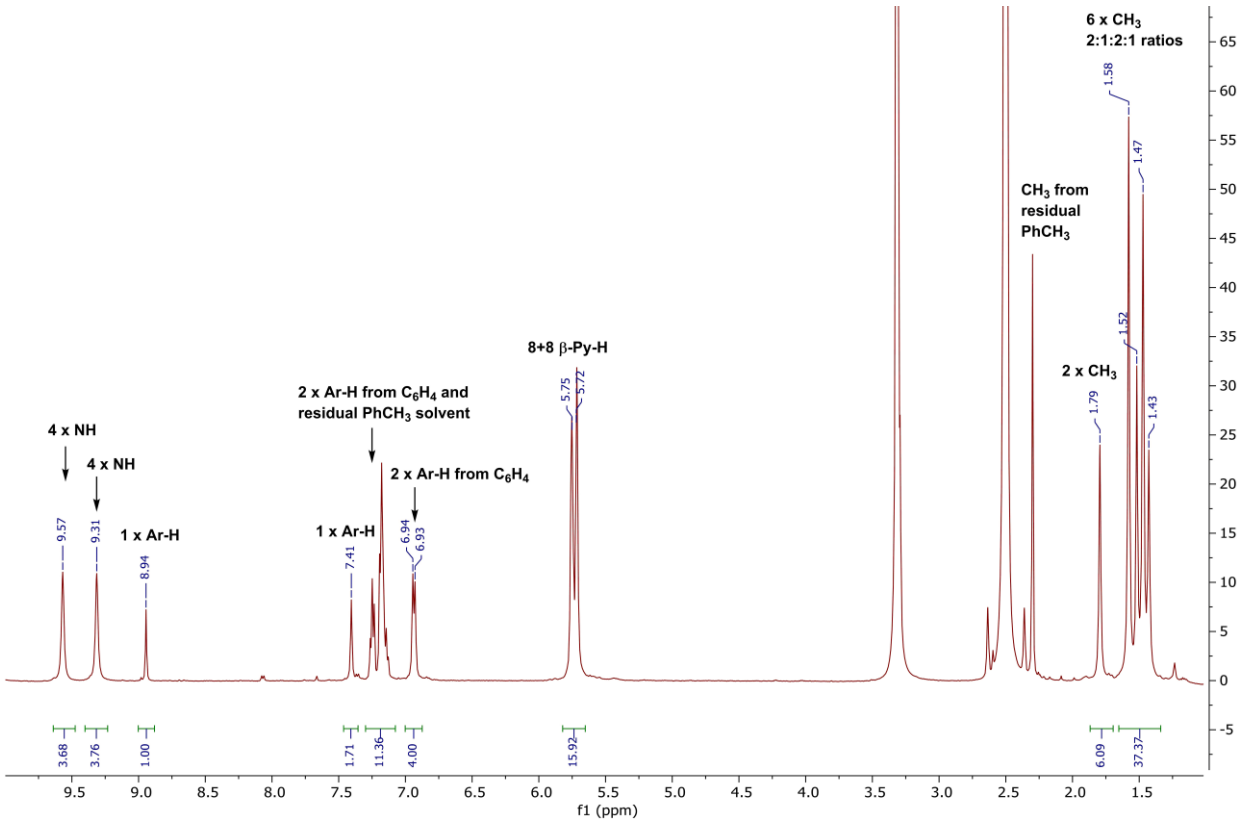

Figure S8a. ^{1}H NMR (500 MHz, DMSO-d_6) for compound **10** with assignments.

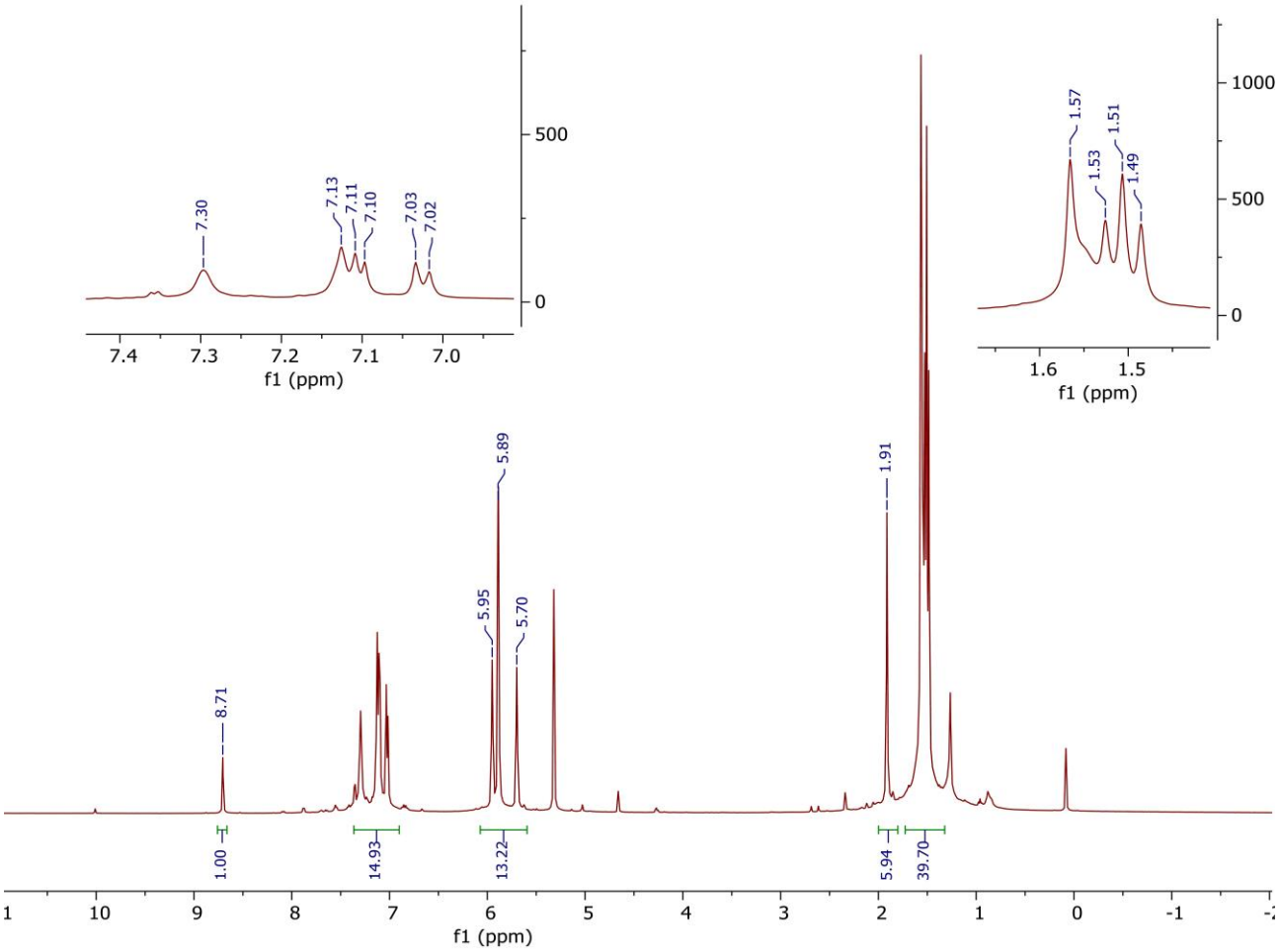

Figure S8b. ^{1}H NMR (500 MHz, CD_2Cl_2) for compound **10**.

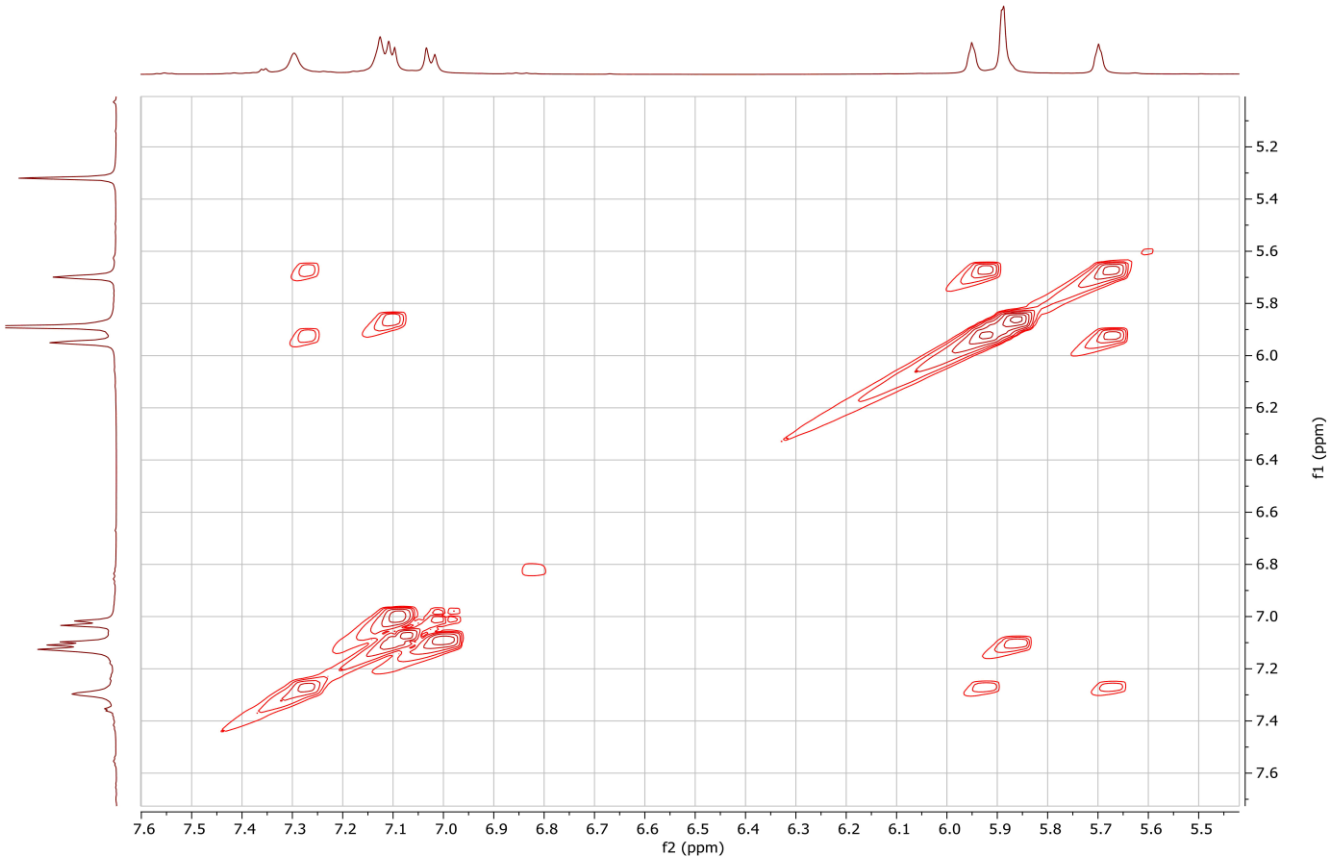

Figure S8c. COSY (500 MHz, CD_2Cl_2) Partial spectrum for compound **10** showing the correlation between the pyrrole b-CH resonances and the NH resonances contained in the signals system at 7.00-7.35 ppm.

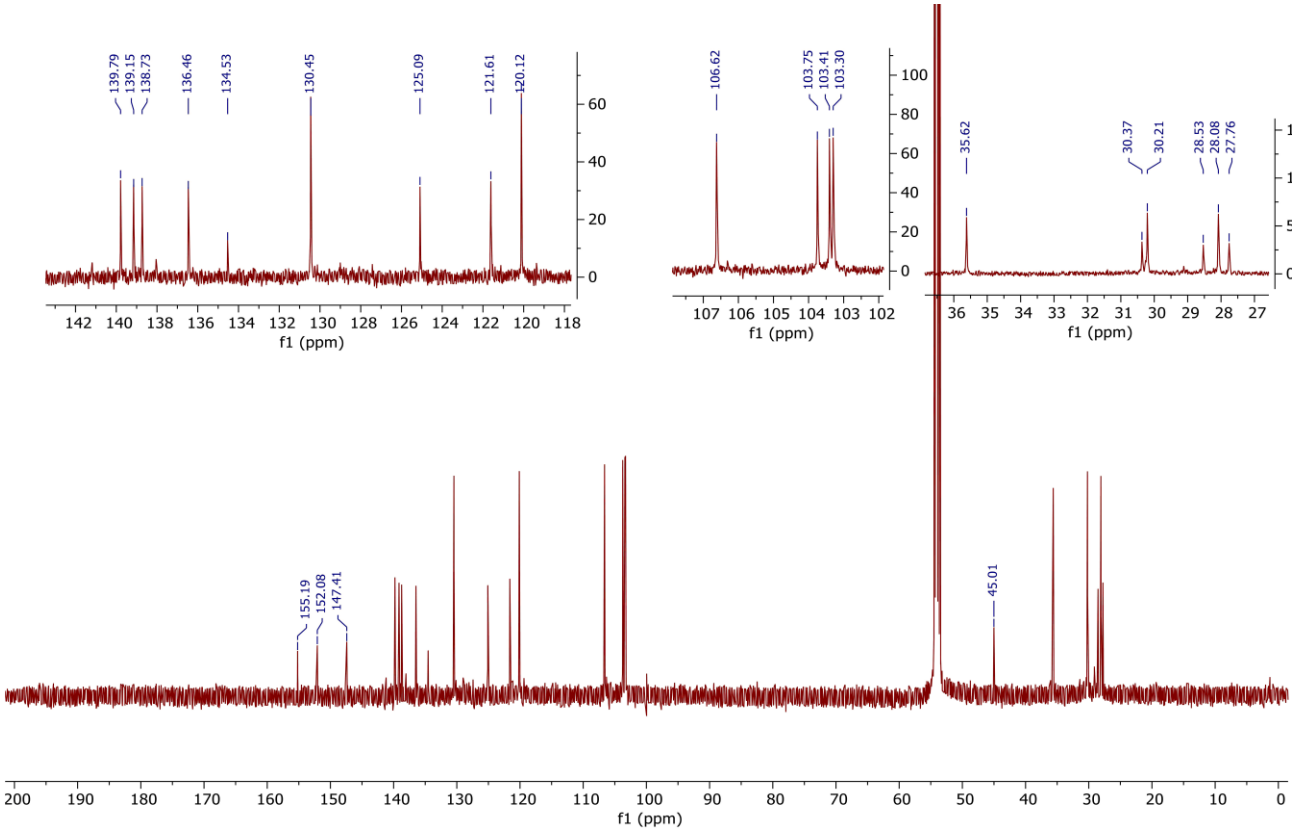

Figure S8d. ^{13}C NMR (500 MHz, CD_2Cl_2) for compound **10.**

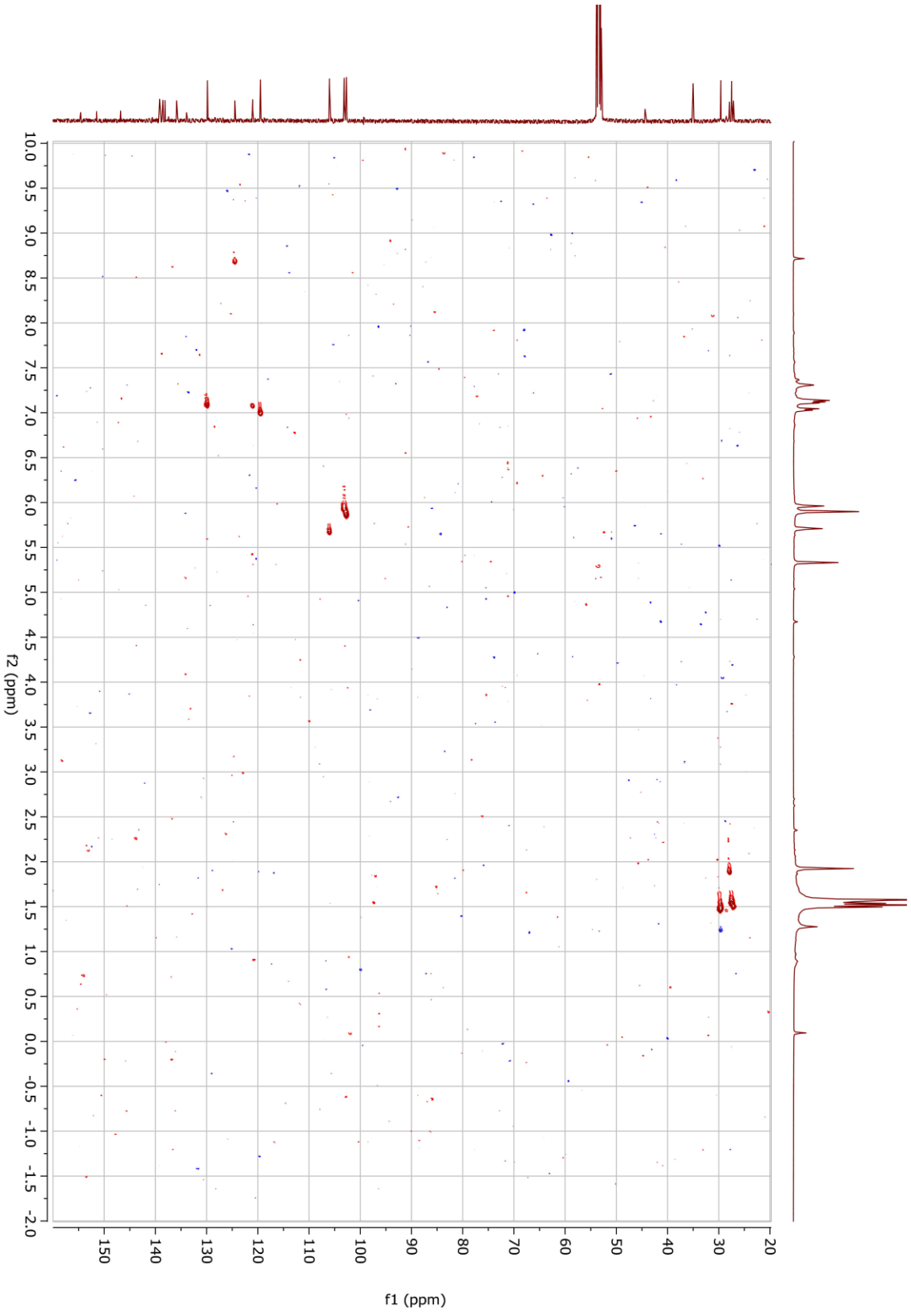

Figure S8e. HSQC (CD_2Cl_2) for compound **10.**

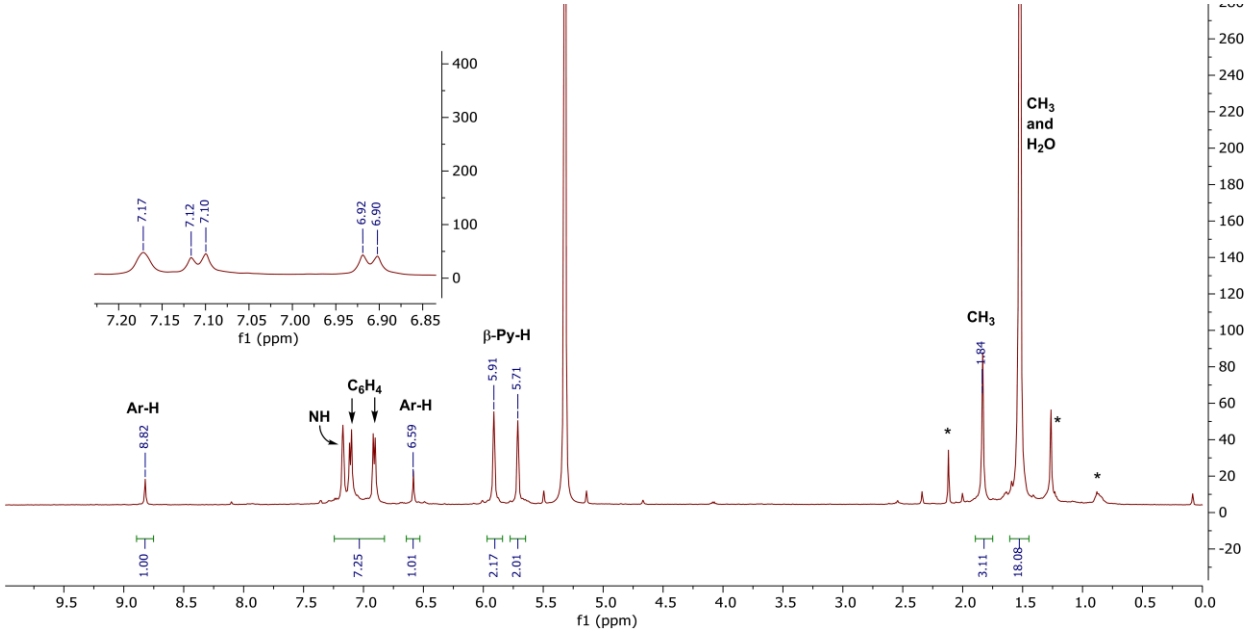

Figure S9a. ^{1}H NMR (500 MHz, CD_2Cl_2) for compound *anti-anti-anti*-**11.** * Solvent impurity.

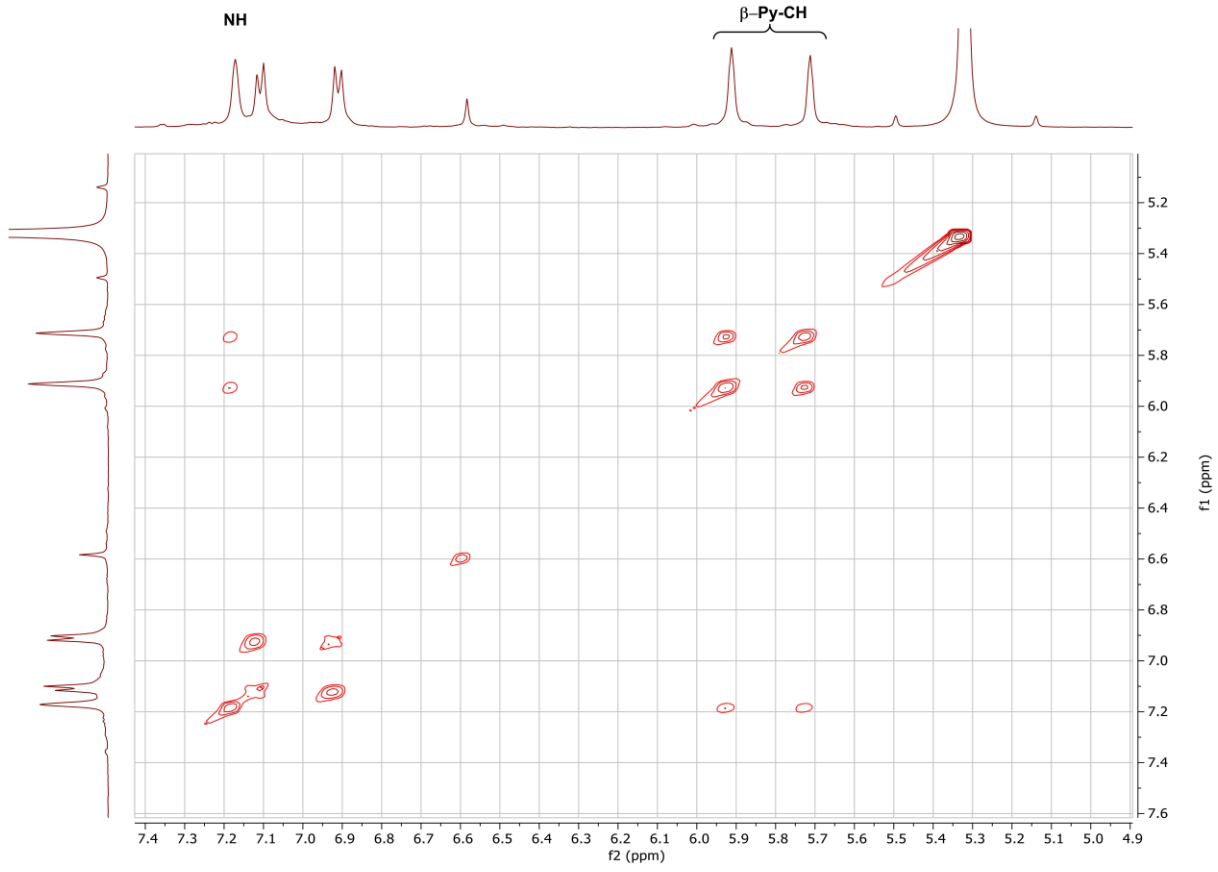

Figure S9b. ^{1}H NMR COSY (500 MHz, CD_2Cl_2) Partial spectrum for compound *anti-anti-anti*-**11** showing the correlation between the pyrrole b-CH resonances and the resonance at 7.17 ppm for the NH units.

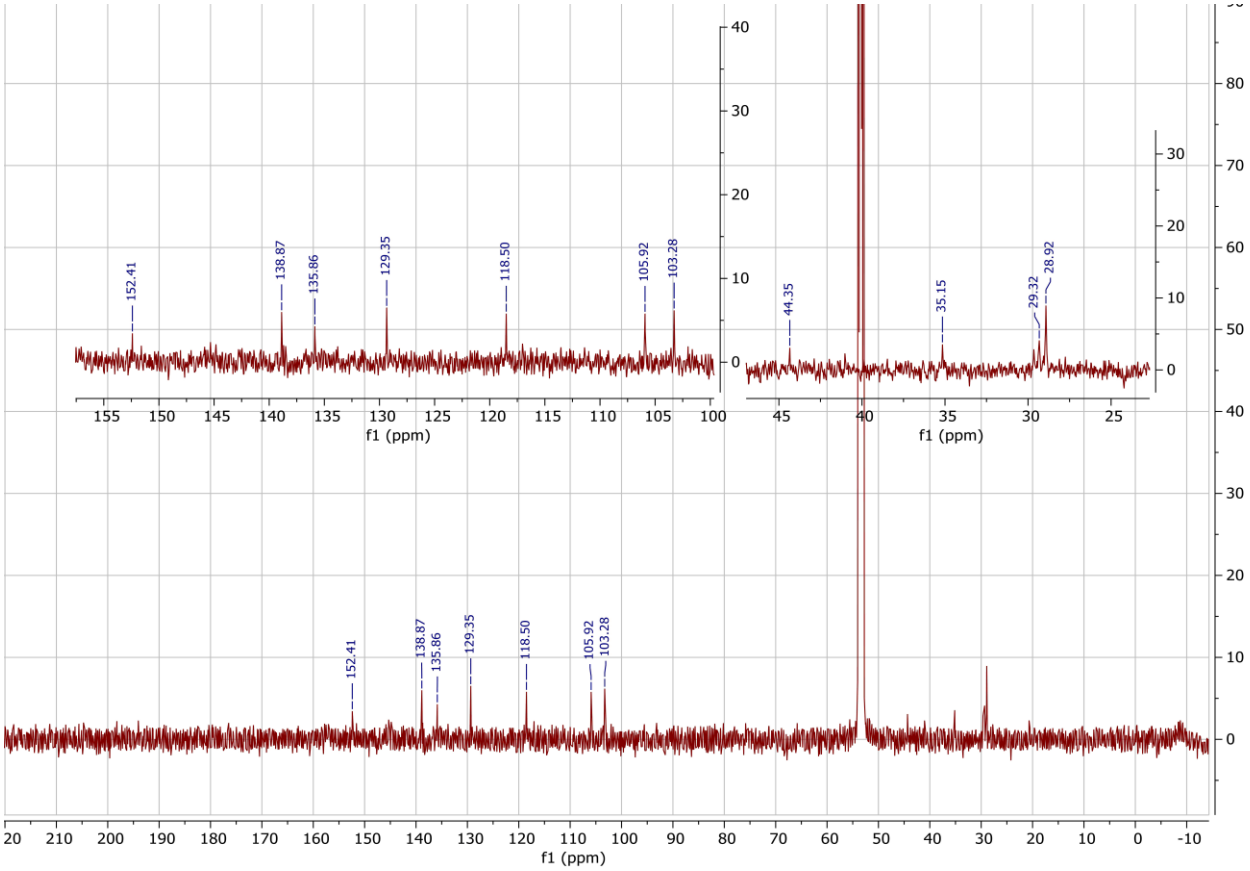

Figure S9c. ^{13}C NMR (125 MHz, CD_2Cl_2) for compound *anti-anti-anti*-**11.**

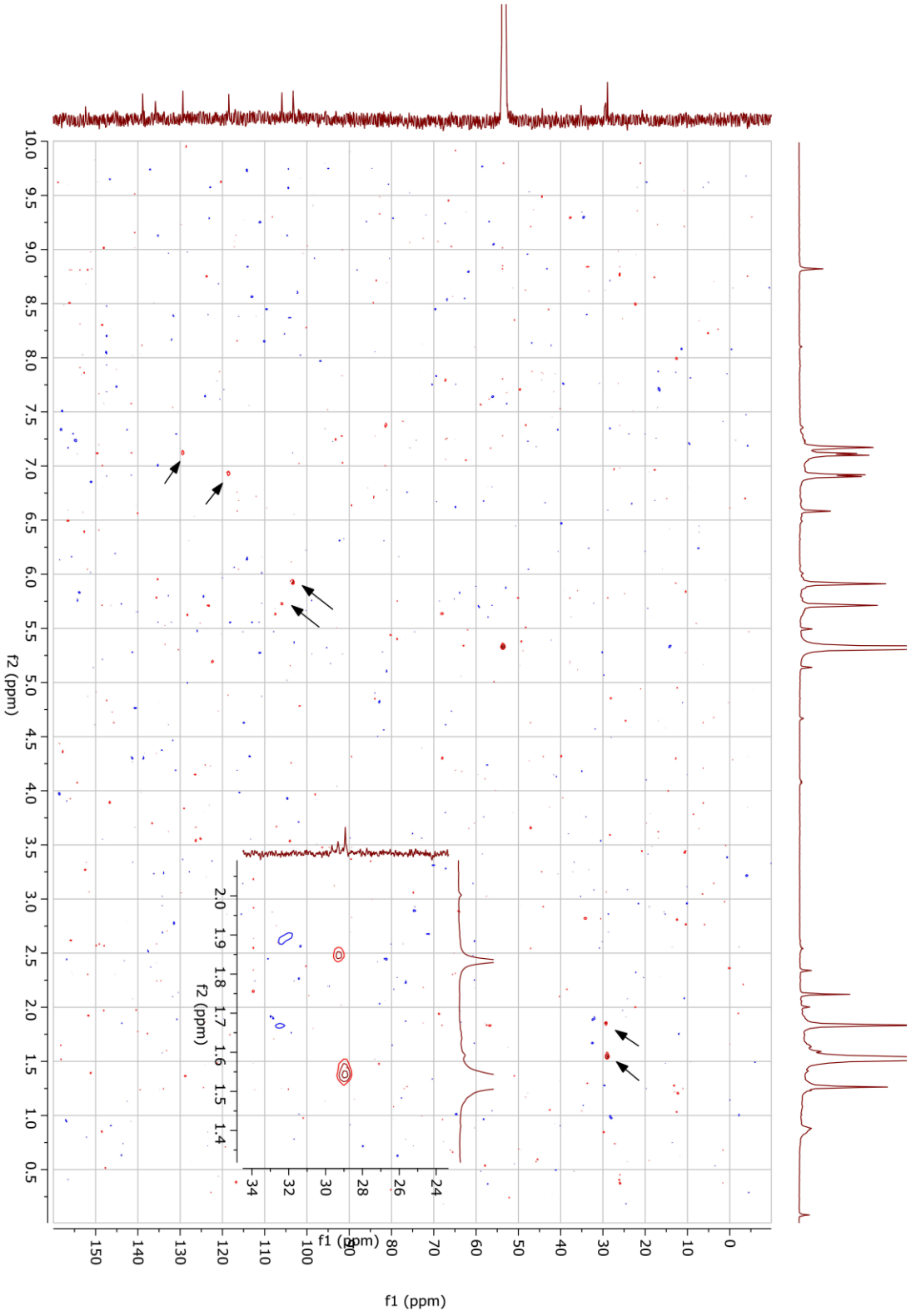

Figure S9d. HSQC (CD_2Cl_2) for compound *anti-anti-anti*-**11.** The arrows are to evidence the correlated signals (red dots) in the noisy background. The inset expansion shows that the strong resonance at 1.52 pp contains the four symmetry-related CH_3 units under the water signal.

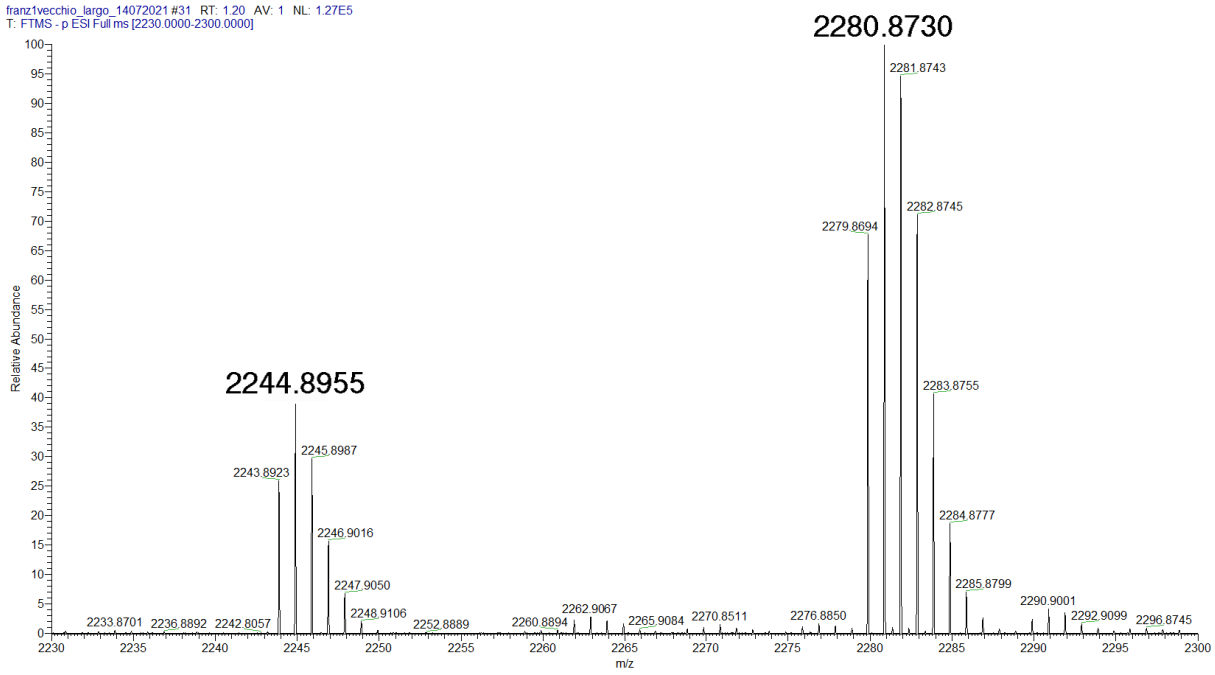

Figure S9e. ESI-MS for compound *anti-anti-anti*-**11**. Calculated *m/z* for $C_{132}H_{120}N_{18}O_{18}$: 2244.9028 and for $C_{132}H_{120}N_{18}O_{18}Cl$: 2279.9028.

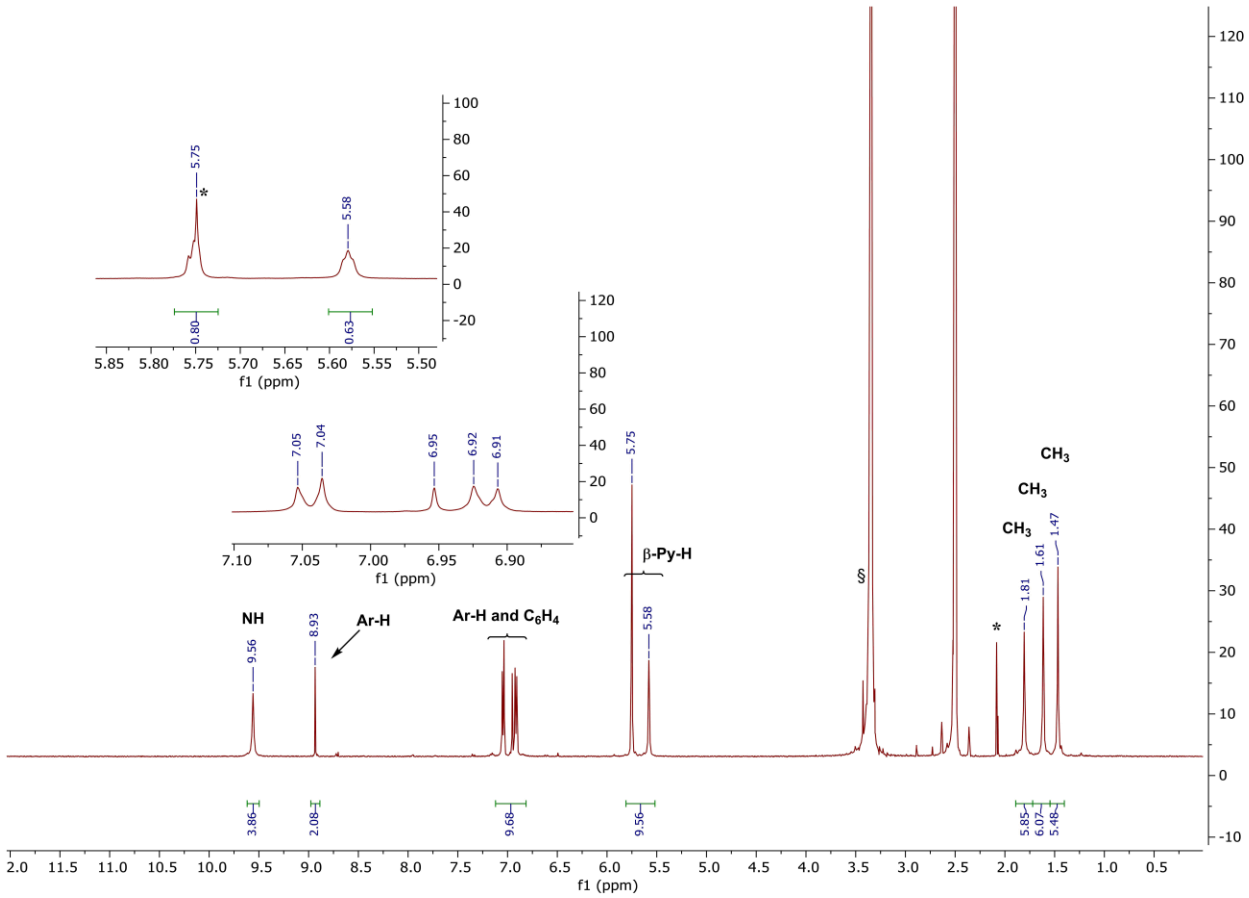

Figure S10a. ^{1}H NMR (500 MHz, DMSO-d_6) for *syn-syn-syn*-**11**. The peak at 5.75 ppm overlapping one set of the b-pyrrole resonances is DCM contaminant in the DMSO solvent; § water; * other solvent impurity (see ref. R1).

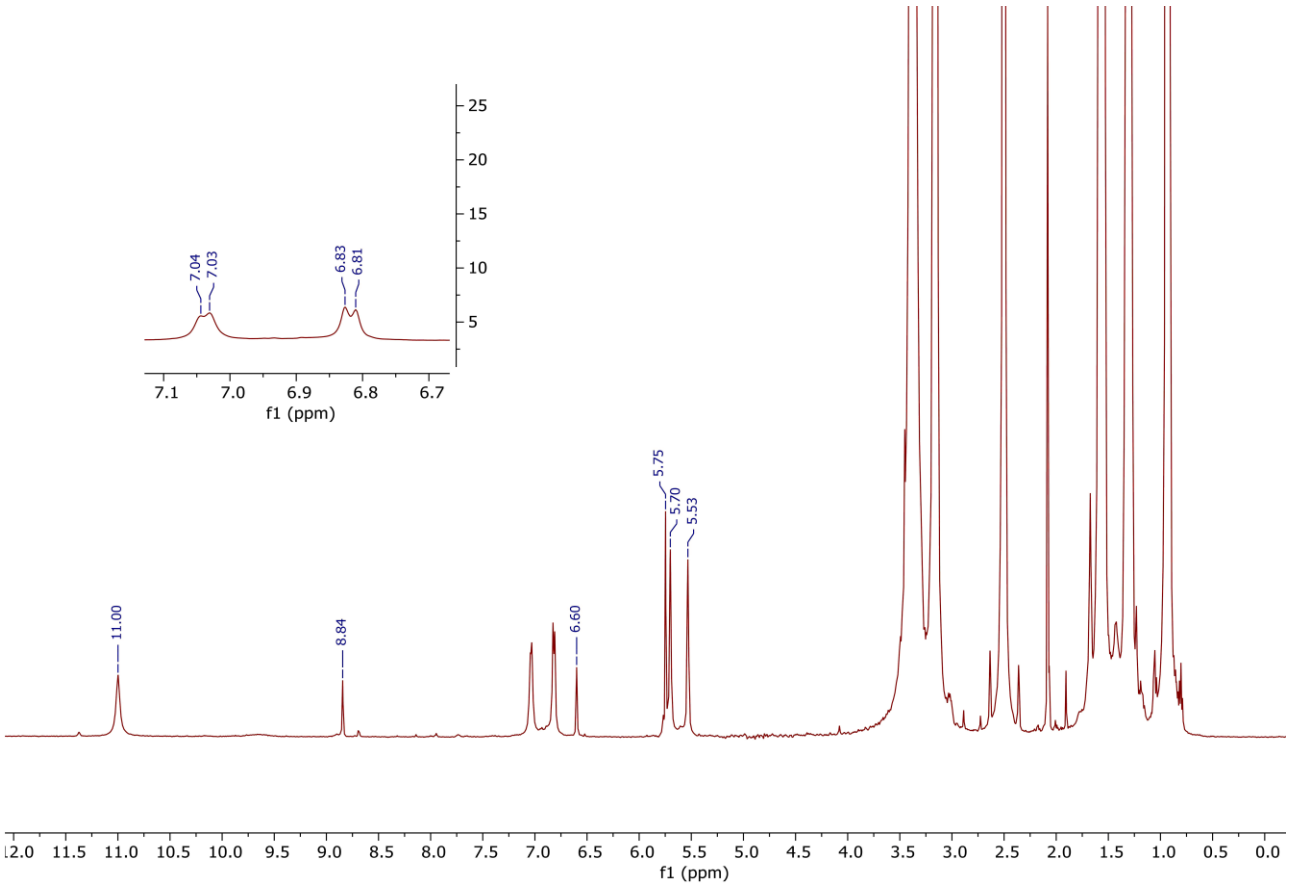

Figure S10b. ^{1}H NMR (500 MHz, DMSO-d_6) for *syn*-*syn*-*syn*-**11** in the presence of molar excess of TBACl. The peak at 5.75 ppm overlapping one set of the b-pyrrole resonances is DCM contaminant in the DMSO solvent (see ref. R1).

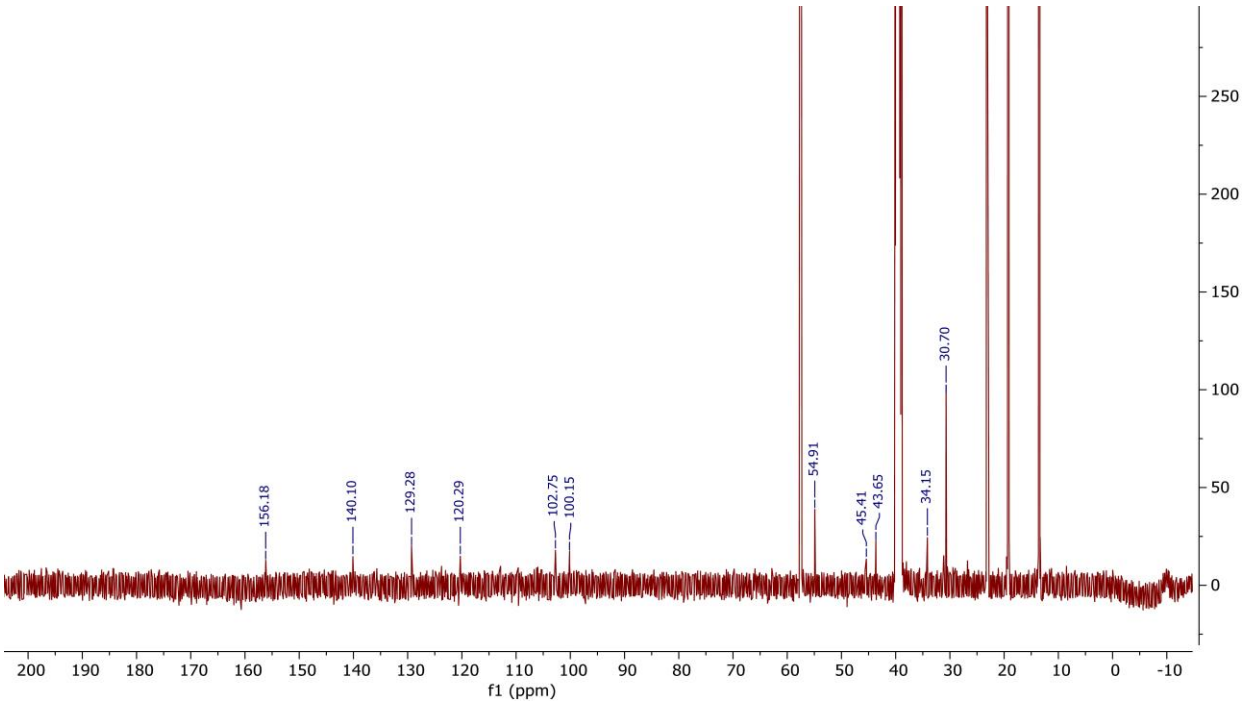

Figure S10c. ^{13}C NMR (125 MHz, DMSO-d_6) for *syn-syn-syn*-**11**. The peak at 54.91 ppm is DCM.

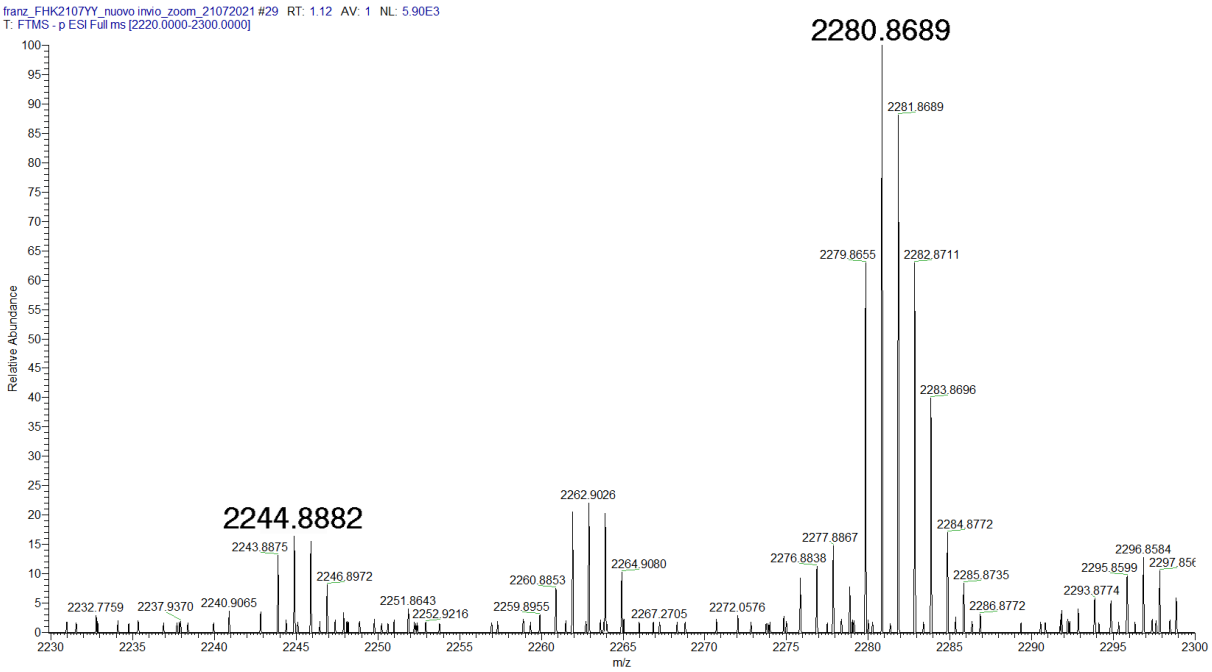

Figure S10d. ESI-MS for *syn-syn-syn*-**11.** Calc. *m/z* for $C_{132}H_{120}N_{18}O_{18}$: 2244.9028 and for $C_{132}H_{120}N_{18}O_{18}Cl$: 2279.9028.

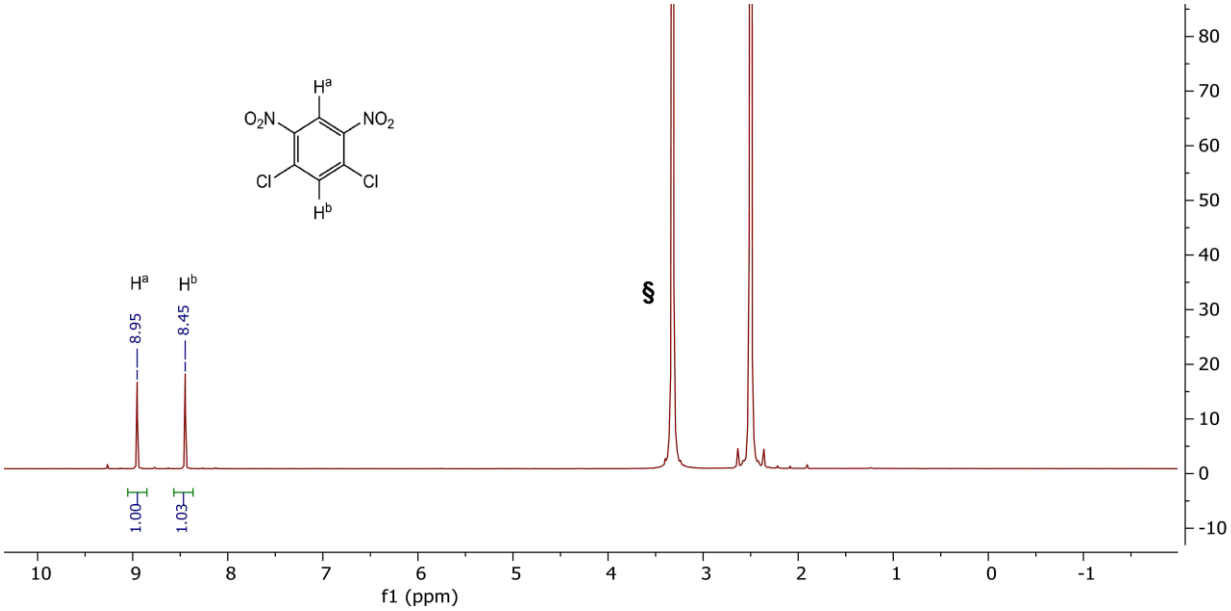

Figure S11a. ^{1}H NMR (DMSO-d_6) for 1,3-dichloro-4,6-dinitrobenzene **9.**

References

R1 Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176-2179. https://doi.org/10.1021/om100106e

